Chem Ed

EDITORIALLY SPEAKING

"Soviet Commitment to Education," the report of the Government's education mission to the Soviet Union should be required reading for all Americans. The document, available from the Government Printing Office for 70 cents, puts into sharp focus the differences between our system and that under the new Soviet "Law on Strengthening the Ties of School with Life and on the Further Development of the System of Public Education in the U.S.S.R." The best use of our space will be to quote and let our editorial urging shout from between the lines. Since the report studiously avoids comparisons with the United States system, we hope the danger of quoting out of context is minimal.

A nation committed:

The one fact that most impressed us was the extent to which the nation is committed to education as a means of national advancement. In the organization of a planned society in the Soviet Union, education is regarded as one of the chief resources and techniques for achieving social, economic, cultural, and scientific objectives in the national interest. Tremendous reponsibilities are therefore placed on Soviet schools and comprehensive support is provided for them by all segments and agencies of Soviet society. . . . It is generally conceded that from 10 to 15% of the total national income is channeled into education of all types.

One of the leading Soviet educators told us, "We believe in a planned society; you believe in individual initiative. Time will tell."

Teacher education:

In the preparation of both elementary and secondary school teachers, there appeared to be an increasing emphasis on solid subject matter content, with less on pedagogy. . . . It is estimated that Soviet teacher trainees spend 40% of their time on preparation of their major subject, 15% on technological application of their specialty, and 15% on the specific method of teaching their major subject. The remainder is divided among general pedagogy, psychology, foreign languages, physical education, and political indoctrination.

Soviet teacher educators consider practical work, that is—observation of teaching, student participation in classroom activities, and practice teaching—to be of the highest importance.

Five years of Soviet teacher training add up to about twice the number of classroom and practice hours as a five year course in the U. S.

Out of approximately five students who apply for admission to an institution of teacher education, one is accepted.

Science education for Soviet children:

The State pays particular attention to the education of scientific workers. It provides for their early years of scientific education and training, encourages them in various ways, and helps them develop in the science field. Pupils without the ability or talent to become scientists use the scientific training they receive as a base for a polytechnical education which prepares them for industrial work.

Science education begins in the kindergarten. There a groundwork for scientific habits in the observation of natural phenomena and plant and animal life is laid before they enter the general school. . . . . Natural science subjects occupy an important place in the study plan. Particularly important is physics, which aims at acquainting the pupil with natural phenomena and the basic principles of production processes.

The study of chemistry begins in the seventh grade with elementary instruction on substances and their transformations; on atomic and molecular studies and the principal laws of chemistry; on oxides, bases, acids, and salts; and on the properties of oxygen, hydrogen, the air, and water. In grades 8, 9, and 10 a systematic course calls for the study of chemical elements according to the periodic table as well as a study of their combinations.

Demonstration experiments are designed to point up the industrial aspects of the subject by emphasizing the chemical basis for obtaining substances in industrial production. For this purpose the students do laboratory and practical work and visit local chemical plants.

The Academy of Sciences:

The most dynamic element in Soviet education and technology appeared to be the institution called "The Academy of Sciences." By sciences Soviet educators mean all branches of knowledge—the humanities, the social sciences, and the natural sciences.

It was of special interest to note the virtually unlimited support for basic research that the Soviet Union is providing through the U.S.S.R. Academy of Sciences and the Republic academies. Apparently, the Soviet Government considers basic research to be the most practical investment it can make. This attitude, along with the high prestige accorded brain power in the Soviet Union makes the Academy of Sciences the most powerful scientific institution that many of us have ever known.

Conclusions:

The strongest impressions we retain include the zeal of the people for education and the rapidly increasing degree of educational opportunity.

In the light of all we saw, we cannot stress too firmly our conviction that our nation must never forget nor underestimate the power and potential of education.

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Fifty Foreign Languages at *Chemical Abstracts*

That foreign languages should be important to *Chemical Abstracts* might well be guessed by everyone who reads this paper. But the problems they bring throughout the system may not be so obvious. A review of how foreign languages are dealt with at *Chemical Abstracts* may be of interest in itself and may also provide information of value to others who must face the same problem.

Languages Used in Abstracting

The following list shows the languages in which we know that chemical information reaches publication, and with which, consequently, we must deal:

Afrikaans	Gaelic	Norwegian
Arabic	Georgian	Persian
Armenian	German	Polish
Azerbaidzhani	Greek	Portuguese
Bohemian[2]	Hebrew	Romanian
Bulgarian	Hindi	Russian
Chinese	Hungarian	Russian (white)
Chinese (modern)	Icelandic	Serbian
Croatian	Indonesian	Siamese
Danish	Interlingua	Slovak
Dutch	Italian	Slovenian
English	Japanese	Spanish
Esperanto	Javanese	Swedish
Estonian	Korean	Turkish
Finnish	Latin	Ukrainian
Flemish	Latvian	Welsh
French	Lithuanian	Yiddish
	Macedonian	

A count has been made on the Volume **52** (1958) abstracts in *Chemical Abstracts* to determine the frequency of occurrence of these languages. Every column in Volume **52** which ended in a "1" was counted, giving a 10% sample. Only articles (not patents) were included, and "parts" of an abstract, usually from a series of papers, were counted separately. The results of this count are presented in Table 1.

Table 1

Language	Number of abstracts	Percentage
English	4823	50.49
Russian	1605	16.80
Azerbaidzhani 2		
Bulgarian 14		
Ukrainian 19		
White Russian 4		
German	928	9.715
Japanese	583	6.10
French	524	5.485
Italian	342	3.58
Bohemian	155	1.62
Polish	145	1.52
Spanish	97	1.015
Romanian	78	0.816
All others	272	2.85
	9552	99.991

The omnibus entry includes articles from Hungarian, Chinese, Serbo-Croatian,[3] Portuguese, Dutch, Scandinavian (combined), Finnish, Greek, Latvian, Afrikaans, Estonian, Gaelic, Hebrew, Turkish (in that order), and 29 *undetermined*. The latter arise mainly from abstracts we copy out of other abstracting periodicals; it is not always possible to tell what the original language was.

It is worth pointing out that the 10% sample from only one annual volume turned up 30 different languages.

Some earlier data of a more restricted sort have been reported by Boig and Howerton (*1*).

An interesting comparison can be made with *Current Chemical Papers*, which covers a restricted number of chemical journals in pure chemistry. Each citation in the listing gives also the original language. A 10% sample of the 1958 volume of *Current Chemical Papers* gave the results seen in Table 2.

Here the "All others" includes (in rank order) Spanish, Dutch, Hungarian, Chinese, Scandinavian, Ukranian, Finnish, Portuguese, and Serbo-Croatian.

A few other analyses of language sources have appeared in the literature. The most directly comparable concerns the medical literature; it appears in an excellent article by Brodman and Taine (*2*).

Table 2

Language	Number	Percentage
English	1505	58.74
German	318	12.41
Russian	310	12.10
French	137	5.35
Japanese	91	3.55
Bohemian	66	2.58
Italian	43	1.68
Polish	31	1.21
Romanian	17	0.66
All other	44	1.72
	2562	100.00

A paper presented at the 135th National Meeting, American Chemical Society, Boston, Massachusetts, April 6, 1959.

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[2] For the purposes of this paper, Bohemian is preferred as a name over Czechoslovakian.

[3] Although Serbian and Croatian are separate languages, they were counted as one for purposes of our survey.

The data tabulated there include these figures (Table 3):

Table 3

Languages	Percentages
English	37.3
German	13.0
French	12.9[4]
Japanese	7.8
Italian	7.5
Spanish	6.2
"Polylingual"	3.3
Russian	3.1
Portuguese	1.5
Polish	1.0
All others	6.4
	100.0

The "All others" includes (in rank order) Dutch, Bohemian, Hungarian, Serbo-Croatian, Chinese, Danish, Swedish, and several more.

Other disciplines such as psychology (*3*) and biology (*4*) have also been concerned with this problem. A good general book on the language problem in science has been edited by J. E. Holmstrom (*5*).

General Language Problems

Languages are one of the areas of concern to the editors of *Chemical Abstracts* in the preparation of the semimonthly issues, in the preparation of Author and Subject Indexes, and in the preparation of the *List of Periodicals Abstracted*. Some of the problems are unique to each of these activities and will be enumerated later under the discussion of each activity, and some of the problems are involved in several phases. These latter problems will be discussed now.

Transliteration, as compared to translation, frequently presents problems. The difficulty here lies in the fact that there are several systems in current use for transliteration from one alphabet to another. For instance, in the transliteration of an author name from Russian to German one would frequently find the use of "wsky" as an ending. Transliterating by the system used by *Chemical Abstracts*, one ends up with "vskiĭ" with a breve over the second "i." Or consider the case of transliteration of a Chinese name into Russian, followed by a subsequent transliteration into English. Thus, standard systems of transliteration not only of author names, but also of proprietary names and names of places, are needed.

Another problem, and one that is probably recognized without too much hesitation, is that of translation. *Chemical Abstracts* publishes all information concerning an article that it has abstracted in English, with the exception of the journal reference and the name of the laboratory at which the work was done. Thus, we are dependent upon abstractors not only for a good, sound abstract, but also for a proper translation of the title of the paper. A typical example in this field follows: Patterson's "German-English Dictionary for Chemists" gives as the English equivalent of "Braunkohle" either "brown coal" or "lignite." According to our expert in coal, Dr. Fieldner, of the U.S. Bureau of Mines and Section Editor since 1921 of Section 21 (Fuels and Coal Products), there is a great distinction between these two. Dr. Fieldner has stated that the usual material found in Germany is brown coal, not lignite. Thus, *CA* editors have a memorandum (one of many) which cautions them to question the use of the word "lignite" when used in abstracts of German papers.

Editors, whether they are working with manuscript proof or Author Index proof are bothered by the proper division of words from foreign languages. Many times the printer will write on the margin of a galley "division OK?" The best solution to this problem is to consult a person who knows the language fluently; however, this is not always possible. On the other hand, one can learn some simple rules or can try to pronounce the word. Thus, no one would approve of this type of division, although I have actually seen it in proof: Schw-artz. Mr. Clouser (private communication) of the Hercules Powder Company Technical Information Service has called our attention to Ostermann's (*6*) work on foreign languages for use of printers, librarians, and bibliographers. Here rules for division of 150 languages are given.

In alphabetizing material from foreign languages, one runs into a problem of gender and case which must be considered.

Fortunately, all of the above problems are becoming easier to solve at *Chemical Abstracts;* the recent increase in staff has brought with it many who possess unusual language abilities. A survey of these abilities, made in October 1958, showed that the staff was capable of reading or translating 23 different languages. One of our editors was listed for 13 different languages.

Language Problem in Acquisition and the Library

The *special* problems of language start with acquisitions and library routines. Received material has to be identified as to language, often by clerical workers. Many journals have no Latin characters in them at all. In this situation we have been helped by the procedure described by Clouser and Skolnik (*7*). There is also a useful and fascinating book which gives samples of over 800 languages in printed form. More than 80 alphabets are represented (*8*). The newer version of this reference gives samples of 1008 languages.

Journals frequently have their titles given in several languages. An example is: *Soproni Műszaki Egyetemi Karok, Bányamérnöki és Földmérőmérnöki Karok Közleményei*, which prints its title on the cover in Hungarian, German, English, and Russian. A recent number had articles printed in only English and German. With the articles thus printed in different languages, it sometimes takes close inspection to identify the correct location in our "Receiving" records.

Capitalization in *CA's List of Periodicals* (*9*) has been influenced by language. Thus, the first word and all nouns will be capitalized in the title of a German periodical. Other languages with definite rules of procedure are Croatian and Bohemian (Czech). For transliterated titles, all principal words are capitalized.

Language Problems in Assignments and Abstracting

Once the library has procured and recorded a journal, it is turned over to the Assignment Department. This

[4] Corrected figure. Private communication from Mr. Taine.

department is charged with selecting articles of chemical interest suitable for inclusion in *Chemical Abstracts*, with the further selection of the proper abstractor, and with the preparation of an assignment card to that abstractor. The work is carried out by several chemists assisted by clerical workers.

Material in Russian is immediately separated from all other material since one of the staff chemists is Russian-born and handles that language with ease. At the same time he can handle Ukrainian, Bulgarian, and White Russian. Armenian and Georgian also go to this worker although here he is dependent on Russian summaries. All other languages go to a chemist, native American, with a reading knowledge of French and German. French helps with other romance languages, German with those of Teutonic origin. This leaves the Balto-slavic groups as a problem. In actual fact, however, many of the journals which are received at *Chemical Abstracts* which are not in English, German, French, or Russian carry at least the title of the article in one of these languages and sometimes carry even lengthy summaries in several languages. This is, of course, helpful. It permits the assigner to select the articles of chemical interest and to determine what field of chemistry is involved. As far as is known, there is only one English-language journal received at *CA* that carries summaries or titles in a foreign tongue. That is the British periodical, *Foundry Trade Journal.*

There are several multilingual journals carrying the same article in English plus another language.

Japanese journals, in Japanese, are handled for *CA* by a group in Japan. An occasional article in Japanese can be assigned from the *Chemical Abstracts* office if there is a summary or title in a language using the Latin or Cyrillic alphabet. Of course the author name(s) must be so given also. Material coming from the Chinese mainland is divided by the assignment group into two sections. The section without Latin or Cyrillic tables of contents or the equivalent is assigned as a whole journal. That material which does have table of contents, or equivalent, in either the Latin or Cyrillic alphabet is processed in the usual manner.

Naturally, a decision as to the language involved is of the greatest importance. Recognition of the country of origin, or the city of publication, or the university from which issued is a big help. Questionable cases are usually settled by reference to the article by Clouser and Skolnik (*7*). Again, recourse to language specialists at *Chemical Abstracts* or the Ohio State University is always helpful.

After the language and field of chemistry have been determined, selection of the abstractor is made. Unfortunately, we do not have a specialist in each of the 50 languages for each of the 700 or more categories of chemistry into which the records are divided. Thus, in Finnish, as an example, a paper in colloid chemistry would be assigned to an abstractor with a command of Finnish who has expressed an interest in physical chemistry. In English, on the other hand, such an article would go to a colloid chemist. One can never jump the boundary of language, unless it be from Dutch to Afrikaans, whereas one can always go from the more specific classification of chemistry to a general one.

Procurement of abstractors in various fields and languages is a major item of concern to the Assignment Department at *CA*. As the library finds more and more journals from a certain geographic area, we find that there are more and more articles to be assigned in some language. Current shortages exist in Russian (a perennial problem), Chinese, Polish, Bulgarian, Bohemian, and Hungarian. This does not mean that abstractors for other languages or even English are not needed. Interested persons should write to Chemical Abstracts Service, The Ohio State University, Columbus 10, Ohio.

Assignment cards are typed for each article. Information on the card includes name of abstractor, name of author(s), title of article in original language, journal reference to include language of article if this is not obvious from title of journal, and address of author(s) if article is in English. *Naturwissenschaften* is a German-language journal but publishes occasional articles in English. Thus, for an English article in the above journal, the reference would read: *Naturwissenschaften* **45**, No. 13, 412–17 (1958) (in English). The typists must be able to recognize common languages; they must be able also to distinguish between authors' academic degrees and titles, as compared to names and initials.

Another language problem that assignment typists have is to recognize the main title, as compared to a subtitle in an article which is one of a series. Sometimes this information about series is given as a footnote; sometimes the article will say: "Study on Alkylation, Part III of Properties of Cycloalkanes," while other times the title will be: "Properties of Cycloalkanes. III. Study on Alkylation." Remember, this is in French, German, Spanish, etc., not in English. No clerical help available can read the 50 languages with which we are concerned today.

Language Problems in Editing Manuscript

In editing work, one must keep in mind that in many instances English is the foreign tongue to the abstractor. Much of *CA* abstracting is done by individuals selected primarily for their knowledge of chemistry and a foreign language and secondarily for their ability to write clear and concise English. We have noticed in the last few years a decided improvement in the quality of the abstracts received at the Editorial Office. This, we believe, can be attributed to two factors: in the first place, abstractors are continually gaining experience and becoming better acquainted with the requirements for a good abstract; and in the second place, in many parts of the world English is becoming a more common language. In any event, use of "broken English" by the abstractor still requires additional editorial time.

In many cases foreign patents have been abstracted for *CA* by individuals at the patent office of the foreign country. This has saved *CA* the cost of purchasing and assigning patents but has resulted in abstracts that were prepared by other than specialists in the field. Editors have noticed this lack of complete knowledge by the abstractor, coupled with poor terminology. Because of the growth of the patent literature, *CA* is assigning more and more of the patents from the Columbus office.

The editorial staff has noted several general defects concerning the quality of abstracts prepared from foreign language articles which might be enumerated here:

The abstracts are prepared by nonspecialists; that is, the abstractor was selected for his language ability, not for his knowledge of the field.

The abstractor uses archaic words; this happens because dictionaries are not so up-to-date as one would like.

The stress at present seems to be on production of English–Foreign language rather than on Foreign language-English dictionaries.

The organism names selected by abstractors are not in line with the common usage of *CA*. Thus, corn and maize are confused.

Some abstracts published by *CA* are taken from other abstract journals such as *Referat. Zhur.*, *Khim.* or *Biol. Abstr.*, etc. These "copy" abstracts are no better than the abstracts from which they are copied. Thus, it can happen that the difficulty becomes compounded.

Organic nomenclature problems arise from faulty translations. The article as abstracted may make good sense, yet does not present the true story of what the author actually did. This type of error is extremely difficult to catch in editing. Thus, the author may have started with ethyl phenylacetate. This was translated by the abstractor as phenylethyl acetate or phenylethylacetic ester. Naturally, there is a big difference here. These errors can creep in even from such common languages as German and French.

Language Problems in Author Indexing

Definitive rules have been adopted by the *Chemical Abstracts* office with regard to use of capital or lower case letters for names containing von, van, van der, etc. These depend on the country in which the individual resides. Thus, in Holland the name is Diji, H. van, alphabetized at D; in America, Van Diji, H., alphabetized at V. What does one do if this Dutch gentleman comes to the U.S. on a postdoctoral fellowship and publishes some work in an American journal from an American University? Similar problems exist with the use of de, di, le, la, etc., in names.

The major ones are involved with transliteration (mentioned earlier) or with double names or with such things as the distinction between Latvian and Russian spelling of the same name.

Spanish names are indexed under the double name, i.e., a Spanish patent at *CA* **51**, 5392*b* was issued to Manuel Perez-Balsera Cabellero, among others. This work in the Author Index for Volume **51** will be found at Perez-Balsera Cabellero, M. On the other hand, Portuguese names are indexed under the single last name. A paper (*CA* **51**, 14300*c*) on cane molasses, published in Brazil, was written by several authors including Nancy de Queiroz Araujo. Portuguese is the native language of Brazil, thus this name appears in the Author Index as Araujo, N. de Q.

East Indian names containing Rao and/or Sri are usually placed in the Author Index under the last part of the name unless from experience or from a letter from the author we know better; thus, in Volume **51** there is an author entry Rao, B. C. S. see Subba Rao, B. C.

We do not use "Mrs." unless we have to. Thus, if both Peter M. Bernays and his wife (using the name Mrs. Peter M. Bernays) are chemists, we cannot run the author index entry as Bernays, P. M. or even Bernays, Peter M. We need to know Mrs. Bernays' given name or use Mrs. to distinguish her from her husband. But it is often difficult to recognize a masculine versus a feminine name in Hindi, Arabic, or Chinese. And then what should the Author Index do when Sally Jones suddenly starts publishing as Sally J. Smith? Send a wedding present? *CA* will normally run an entry: Jones, Sally, name changed to Smith, Sally J.

Recently we came upon this problem of author names as varied in transliteration from Chinese into English directly and via Russian:

Chinese characters:	吳汶海	(illegible)
Russian version:	Увэн-Кай	Чжоу Гуан-чжао
Russian transliteration:	U, Ven-Khai	Chzhou, Guan-Chzhou
English name:	Wu, Wen-Hai	Chou, Kuang-Chao

Language Problems in Subject Indexing

The special problems here are mostly ones of deciding what spelling to use. For instance, should all trivial names containing the root "pharm," as in Pharmacy, be changed to "ph," even if the original language used an "f" as in Farmacie? Our decision is to stay with the original spelling.

Another language problem in subject indexing is that of "shop language." By shop language we mean the terms used in a specific industry which may not mean the same as they do in chemical nomenclature. For instance, the drug chlorobutanol is actually 1,1,1-trichloro-2-methyl-2-propanol. Another example: the detergent trade frequently speaks of dodecylbenzenesulfonic acid, meaning benzene sulfonic acid to which is attached a 12-carbon sidechain. Dodecyl in chemical nomenclature actually means the normal 12-carbon chain; rarely does the trade mean the normal dodecyl group. Thus, the trade language for the compound is not the same as the index entry. Again, the petroleum industry may speak of octanes; octane to the indexer means normal-octane. The problem here is not one of a foreign language but of another version of English. Compound this by translations from foreign languages, and you realize that subject indexing, too, has its language problems.

Conclusion

We have mentioned some of the difficulties which are encountered in the preparation of *Chemical Abstracts*, with reference to the language problem. By no means have we pointed out all of them; in many cases we merely have suggested possible solutions. A general, but unreachable, solution seems to be the use of technically trained people who have an intimate, up-to-date knowledge of each language. Comments on any points made will be greatly appreciated.

Acknowledgment

At this time we would like to acknowledge the help of many of our colleagues at *CA* who gave generously of their time during discussion periods and who pointed out some of their particular language problems.

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Japanese Organic Chemical Nomenclature

Problems of translation and transliteration

Scientific words are more important as written language than as spoken language. In Japan, Chinese characters and a set of Japanese phonetic letters which is called *Kana* are used in scientific papers, books, and other documents almost exclusively unless they are prepared in foreign languages. The Romanized Japanese writing is not yet popular in scientific literature in spite of effort to propagate it. Naturally, Japan needs a nomenclature in which rules and chemical names are given by Chinese characters and Japanese letters.

Prior to the introduction of the modern sciences, scientific terms and names already existed in Japan, but as foreign scientific information was imported, it was conveyed by foreign words. The foreign words were put into Japanese by the combination of two methods, namely, translation and transliteration. Chinese characters were used for translation. Each of those characters forms a hieroglyph and has a definite meaning as well as a definite pronunciation. Japanese letters, each of which denotes a sound only, were used for transliteration.

Transliteration puts foreign words into Japanese letters with sounds which resemble the pronunciation of the original foreign words. However, foreign words are not, and cannot, be transliterated exactly as they are pronounced in their respective native tongues.

In Figure 1, a set of 51 Japanese phonetic letters is shown in *Katakana* style. The sound of each letter is obtained by combining the consonants at the top line and the vowels at the left column. The vowels are A,I,U,E, and O. Each letter, including N, makes one syllable. Thus, a word like *Shinichi*, when written in Romanized writing, becomes a very confusing one to read because it can be read in two ways, either *Shi-n-i-chi* or *Shi-ni-chi*. Again these are different from *Shinnichi* which is read as *Shi-n-ni-chi*.

There are a few irregular sounds in the S and T columns. They are *Shi* in the S column and *Chi* and *Chi* and *Tsu* in the T column.

Some of the consonants are modified to form voiced consonants. For example, G from K, Z from S, D from T, and B and P from H. Those voiced consonants are distinguished from the original letters by

		K	S	T	N	H	M	Y	R	W	N
A	ア	カ	サ SA	タ TA	ナ	ハ	マ	ヤ	ラ	ワ	ン
I	イ	キ	シ SHI	チ CHI	ニ	ヒ	ミ	イ	リ	ヰ	
U	ウ	ク	ス SU	ツ TSU	ヌ	フ	ム	ユ	ル	ウ	
E	エ	ケ	セ SE	テ TE	ネ	ヘ	メ	エ	レ	エ	
O	オ	コ	ソ SO	ト TO	ノ	ホ	モ	ヨ	ロ	ヲ	

		G	Z	D		B	P
A		ガ	ザ ZA	ダ DA		バ	パ
I		ギ	ジ JI	ヂ JI		ビ	ピ
U		グ	ズ ZU	ヅ ZU		ブ	プ
E		ゲ	ゼ ZE	デ DE		ベ	ペ
O		ゴ	ゾ ZO	ド DO		ボ	ポ

Figure 1.

[1] With permission of the original author, Professor Y. Urushibara, the writer has made some changes in order to make it more understandable to the American people. Those changes include omission of some sentences, rewording, and use of eight figures. However, maximum effort has been exerted to reserve the original content as much as possible.

Presented as part of Symposium on Organic Chemical Nomenclature at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

putting two dots or a small circle at the upper-right corner of the letters.

In Figure 2 are shown some typical methods by which the transliteration is done. Roughly speaking, all vowels are transliterated as short sounds except O in OL or -OSE, and A in -AL. L is transliterated as R, V as B, PH and F as H, TH as T (or S), QU as K, and so on. Some Japanese sounds are expressed by a combination of two letters, one letter and a subscript, as in *Phenyl* or *Phenol.*

Japanese chemical names are formed by mixed translation and transliteration (Fig. 3). For example, acetic acid is translated as *Sakusan,* which means vinegar acid, and butyric acid as *Rakusan,* which means dairy or butter acid. Acetamide is transliterated as *Asetamido,* since there is no corresponding translation for amide. In the case of propionic acid, the word acid (*San*) is translated and propionic is transliterated. Transliteration is used much oftener than translation because many chemical names are derived from words

-OL, -OSE,	オール (Ō RU), オース (Ō SU)
LIGROIN,	リグロイン (RI GU RO I N)
VINYL BUTYRAL,	ビニルブチラール (BI NI RU BU CHI RĀ RU)
ETHYL,	エチル (E CHI RU)
PHTHALO-,	フタロ (HU TA RO)
PHENYL,	フェニル (FE NI RU) (ファ FA, フェ FE, フィ FI)
QUINONE,	キノン (KI NO N) (クァ QUA, クェ QUE)

Figure 2.

referring to things which have not been known previously in Japan. Those words cannot be expressed in the Japanese native tongue.

The transliteration of chemical words has caused much confusion. English, German, and other foreign words were chosen randomly as the origin of transliteration. To make matters worse, the same substance was sometimes called by two or more names which were obtained by the transliteration of foreign names of different languages. Recently one name has been

ACETIC ACID,	酢 SA KU VINEGAR		酸 SAN ACID			
BUTYRIC ACID,	酪 RA KU BUTTER		酸 SAN ACID			
ACETAMIDE,	ア A	セ SE	タ TA	ミ MI	ド DO	
PROPIONIC ACID,	プ° PU	ロ RO	ピ° PI	オ O	ン N	酸 SAN

Figure 3.

KETONE	ケ KE	ト TO	ン N		
ALDEHYDE	ア A	ル RU	デ DE	ヒ HI	ド DO
ESTER	エ E	ス SU	テ TE	ル RU	
BUTADIENE	ブ BU	タ TA	ジ JI	エ E	ン N
BENZINE	ベ BE	ン N	ジ JI	ン N	
BENZENE	ベ BE	ン N	ゼ ZE	ン N	
QUININE	キ KI	ニ NI	ン N		
XYLENE	キ KI	シ SHI	レ RE	ン N	

Figure 4.

selected and the others discarded. In doing so, the most widely used transliterations were adopted, the majority of which are of German origin. Several examples of such words are shown in Figure 4. Ketone is transliterated as *Keton,* aldehyde as *Arudehido,* ester as *Esuteru,* benzine as *Benjin,* benzene as *Benzen,* quinine as *Kinin,* and xylene as *Kishiren.*

At the same time, some rules for transliteration have been provided and English names chosen for the origin of new transliterations. But, if the new English names are composed of old, known words, the names are often transliterated as if they were German.

Another characteristic of Japanese transliteration is disagreement in the number of syllables with English usage. All Japanese letters are voweled sounds except that for N. Therefore, except for N, English consonants have to be translitereated as if they were followed by certain vowels even if they are really not. Most consonants are followed by a light U sound as in *put,* and t and d are followed by a light O sound as in *obey* (Fig. 5). Moreover, composite words are divided

U [PUT], O [OBEY]								
FORMALDEHYDE	ホ HO	ル RU	ム MU	ア A	ル RU	デ DE	ヒ HI	ド DO
PHENOLPHTHALEIN	フェ FE	ノー NŌ	ル RU	フ HU	タ TA	レ RE	イ I	ン N
ETHYLBENZENE	エ E	チ CHI	ル RU	ベ BE	ン N	ゼ ZE	ン N	

Figure 5.

into their components. In this way, the number of syllables in a transliterated Japanese name may be greater than that of the corresponding English name. For instance, formaldehyde is transliterated as *Horumu·Arudehido;* phenolphthalein is transliterated into nine letters and read in eight sounds.

The original nomenclature rules of the International Union of Pure and Applied Chemistry are provided in English and/or French. Direct translation and transliteration of the rules give difficulties because the translated rules cannot be applied directly to Japanese names.

BUTANE	ブ タ ン BU TA N
BUTENE	ブ テ ン BU TE N
BUTYL	ブ チ ル BU CHI RU
BUTANOL	ブ タ ノ ー ル BU TA NŌ RU
DECANE	デ カ ン DE KA N
DECENE	デ セ ン DE SE N
DECYL	デ シ ル DE SHI RU

Figure 6.

Some of the difficulties are shown in Figure 6. In English, butene, butyl, and butanol are derived from butane by changing or adding suffixes. In transliterated Japanese, *ta, te, or ty* is transliterated into one letter and cannot be divided in two letters. Therefore, when deriving butene from butane in Japanese, the second letter has to be changed from *TA* to *TE*. *Butan* becomes *Buten*. Then, the root of the word is lost. Another type of difficulty is met when a suffix which starts with a vowel is to be added to a name ending with N. As mentioned before, the Japanese letter which corresponds to N makes one syllable by itself and cannot form a new letter by being combined with a vowel of the following suffix. If the suffix were forced into combination, the resulting words would become very unnatural at the junction and oftentimes would be incomprehensible. These complications arise from the fact that all Japanese letters are vowelled sounds except that for N and that N makes a syllable by itself. The original rules of the IUPAC could be paraphrased and made into rules which could be applied directly to Japanese names, though they would become very complicated rules.

More complication is seen in the case of decane. Decane, decene, and decyl are transliterated as *Dekan*, *Desen*, and *Deshiru*. The second letters of those words are *Ka*, *Se*, and *Shi*. Those letters do not belong even to the same column of the phonetic letter chart. Actually it is impossible to provide a common rule in the Japanese language to indicate a method of deriving,

PENTENOL	ペ ン テ ノ ー ル PE N TE NŌ RU
2-PENTEN-1-OL	2 - ペ ン テ ン - 1 - オール PE N TE N Ō RU
BUTENYL	ブ テ ニ ル BU TE NI RU
2-BUTEN-1-YL	2 - ブ テ ン - 1 - イ ル BU TE N I RU
1-BUTENE	1 - ブ テ ン BU TE N
BUT-1-ENE	ブ ト - 1 - エ ン BU TO E N

Figure 7.

for example, decene and decyl from decane, without knowing the original words.

The IUPAC rules provide alternatives and arbitrariness to some extent, for example, in the order of mentioning the names of substituent radicals in a compound or in the places for putting the Arabic numerals to indicate positions.

Chemical Abstracts adopts the alphabetical order of radical names. Transliteration of alphabetical order gives Japanese names with no order. A special order of Japanese letters exists, but IUPAC rules do not allow rearrangement of radical names in this order because only two alternative methods are permitted, namely, alphabetic order or the order based on the degree of complexity. It would be troublesome to adopt the order of complexity, because then it would be necessary to provide a rule defining the degree of complexity for all possible radicals. The Japanese have adopted tentatively the *Chemical Abstracts* order in transliteration.

It is sometimes difficult to find a place in a chemical name for putting Arabic numerals to indicate the

COUMALIN COUMARIN	ク マ リ ン KU MA RI N
CARVYLAMINE CARBYLAMINE	カ ル ビ ル ア ミ ン KA RU BI RU A MI N
ACETIC ACID	酢 酸 SA KU SAN
ACETATE (SALT)	酢 酸 塩 SA KU SAN EN
Pb-ACETATE	酢 酸 鉛 SA KU SAN NAMARI
ACETATE (ESTER)	酢 酸 エ ス テ ル SA KU SAN E SU TE RU
ETHYL ACETATE	酢 酸 エ チ ル SA KU SAN E CHI RU

Figure 8.

position of substitution, unsaturation, functional group, etc. The Japanese follow the style of *Chemical Abstracts* as long as it permits a reasonable transliteration.

A numeral prefixed to an entire name causes no difficulty, but one inserted between letters is often a great annoyance (Fig. 7). 2–Penten–1–ol or 2-buten–1–yl can be transliterated without changing the places of the numerals, since each portion of the divided name makes sense, namely, *pentent* and *ol* or *butene* and *yl*.

On the other hand, such an example as but-1-ene is troublesome in transliteration. The word butene is divided into two parts, *but* and *ene*. The former part *but* ends with a consonant *t*. As mentioned before, *t* is transliterated as *To*, therefore, *but* becomes *Buto*. These divided and transliterated parts of a word do not make sense in any Japanese names. Here again, the root of the word is lost, and there are no means of finding *Butan* from *Buto*. The matter becomes worse in more complicated examples, such as bicyclo[2.2.1]hept-2-ene, 5α-androst-1-en-17β-ol, and 5β-pregn-3-ene.

The original forms of Arabic numerals, Greek letters, symbols for elements, capital letters D and L, + and − signs for optical rotation, and other letters

usually printed in italics in English names are also used in Japanese chemical names. The difference between English and American conventions causes some confusion in Japanese nomenclature, but the American system is preferred somewhat because it gives Japanese names with fewer foreign letters.

Although some rules for transliteration have been provided, many problems still remain unsolved. It is difficult or even useless to have foreigners understand them all, but a few examples may be shown (Fig. 8). As mentioned before, no discrimination is made between L and R, or V and B in transliteration. Therefore, some different English words will have the same transliteration, such as coumalin and coumarin, or carvylamine and carbylamine.

A problem of translation may be added. Both the salt and the ester of an acid are called by the same name in English, e.g., acetate from acetic acid. In Japan, most common acids have entirely translated names. To refer to the salt or ester of these acids, the full names of the free acids are used followed by a word meaning salt or ester. For example (Fig. 8), from acetic acid, Sakusan, Sakusan-en (or Sakusan Namari) is obtained for a salt, and Sakusan-Esuteru (or Sakusan Echiru) for an ester. Therefore, such a word as acetate cannot be translated without knowing whether it implies a salt or an ester. Therefore, the word has to be transliterated.

In conclusion, I confess that my serious concern is that Japanese organic chemists do not pay proper attention to nomenclature. If this paper arouses interest in the problems of Japanese organic chemical nomenclature among the organic chemists of the United States and stimulates the attention of Japanese organic chemists, I should be thankful that my efforts are doubly appreciated.

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Use of a Digital Computer for Solving a Complex Chemical Equilibrium

During the course of a study of the radiation chemistry of aqueous ferric oxalate, it was necessary to know the concentrations of the individual chemical species that exist in a dilute sulfuric acid solution of Fe(III) and oxalic acid or oxalate ion. This system is a good example of a chemical system at equilibrium which is described by a series of expressions for acid dissociation and complex formation. Although the individual expressions are simple, they are not mutually independent; hence together they give a family of equations whose solutions by the usual methods require a great deal of labor. Since the services of a large digital computer were available at this institution, it was possible to obtain comparatively rapid solutions to the problem. This paper is intended to point out the applicability of digital computers to chemical problems of this type and the technique by which they are programmed and handled by a computer.

The subjects of these calculations were the solutions made up of combinations of aliquots of ferric ammonium sulfate, ammonium tris(oxalato)ferrate(III), oxalic acid, potassium oxalate, and sulfuric acid. The separate chemical equilibria that pertain, and their constants (*1*), are the following:

$$\frac{[Fe^{3+}]\,[C_2O_4^{=}]}{[Fe(C_2O_4)^+]} = 3.98 \times 10^{-10} = K_7$$

$$\frac{[Fe(C_2O_4)^+]\,[C_2O_4^{=}]}{[Fe(C_2O_4)_2^-]} = 1.59 \times 10^{-7} = K_6$$

$$\frac{[Fe(C_2O_4)_2^-]\,[C_2O_4^{=}]}{[Fe(C_2O_4)_3^{=}]} = 1.0 \times 10^{-4} = K_5$$

$$\frac{[HC_2O_4^-]\,[H^+]}{[H_2C_2O_4]} = 5.95 \times 10^{-2} = K_9$$

$$\frac{[C_2O_4^{=}]\,[H^+]}{[HC_2O_4^-]} = 6.40 \times 10^{-5} = K_{10}$$

$$\frac{[SO_4^{=}]\,[H^+]}{[HSO_4^-]} = 1.60 \times 10^{-2} = K_8$$

These six equations involve ten unknown quantities. The four additional equations are the material balance relationships which are determined by the stoichiometry of any particular solution:

$$[Fe^{3+}] + [Fe(C_2O_4)^+] + [Fe(C_2O_4)_2^-] + [Fe(C_2O_4)_3^{=}] = \text{total iron concentration} = K_1$$

$$[C_2O_4^{=}] + [HC_2O_4^-] + [H_2C_2O_4] + [Fe(C_2O_4)^+] + 2[Fe(C_2O_4)_2^-] + 3[Fe(C_2O_4)_3^{=}] = \text{total oxalate concentration} = K_4$$

$$[HSO_4^-] + [HC_2O_4^-] + 2[H_2C_2O_4] + [H^+] = \text{total available hydrogen ion, excluding water} = K_3$$

$$[HSO_4^-] + [SO_4^{=}] = \text{total sulfate concentration} = K_2$$

The omission of the activity coefficients is justified since all the solutions have approximately the same ionic strength and we are concerned with variation in concentrations more than in absolute values. One should note that the hydrolysis of ferric ion is suppressed either by the acidity or by complex formation so that the hydrolysis equilibrium may be neglected. For similar reasons, the ammonium ion may also be neglected. In addition, it is assumed that the iron

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oxalate complexes are weaker bases than the other bases in the solution.

For convenience, the following substitution of symbols is made:

$[Fe(C_2O_4)^+] = A$	$[HSO_4^-] = F$
$[Fe(C_2O_4)_2^-] = B$	$[H^+] = G$
$[Fe(C_2O_4)_3^{=}] = C$	$[HC_2O_4^-] = H$
$[Fe^{+3}] = D$	$[H_2C_2O_4] = I$
$[SO_4^{=}] = E$	$[C_2O_4^{=}] = J$

A–J are the unknowns, K_1, K_2, K_3, and K_4 represent the material balance sums for a particular case; K_5, K_6, and K_7 the complex ion dissociation constants (*1*); and K_8, K_9, and K_{10} are the acid dissociation constants. All symbols stand for numbers with the dimensions moles per liter. The family of equations that must be solved is then:

$$A + B + C + D = K_1 \quad (1)$$
$$E + F = K_2 \quad (2)$$
$$F + G + H + 2I = K_3 \quad (3)$$
$$A + 2B + 3C + H + I + J = K_4 \quad (4)$$
$$BJ = CK_5 \quad (5)$$
$$AJ = BK_6 \quad (6)$$
$$DJ = AK_7 \quad (7)$$
$$GE = FK_8 \quad (8)$$
$$GH = IK_9 \quad (9)$$
$$GJ = HK_{10} \quad (10)$$

Nature of a Computer

PENNSTAC (Penn State Computer), which was used for the calculations, is a digital computer similar in function to most large digital computers. The computer contains an input unit which can read coded numbers and instructions from a paper tape and store them in the memory. The calculations are done in the arithmetic and logic unit which also incorporates an accumulator for temporary storage of numbers on which operations are performed. The actual mathematical operations are limited to the very simple processes of addition, subtraction, multiplication, division, and a few combinations of these. On instruction, all or any part of the content of the memory may be read out either onto a paper tape or through an electric typewriter as coded numbers.

In order to solve a problem on a computer several preliminary steps must be completed (*2*). First the problem is subjected to numerical analysis in order to express it in a form which will yield the answers after a step-by-step sequence of arithmetical operations. It is then programmed by writing down the complete sequence of steps to be taken. Following this it is coded by writing each number and instruction for the sequence in the form the machine can accept.

The coding system used by PENNSTAC is a two-address code, and instructions are normally executed serially. The *instruction word* is made up of ten digits. The first two digits are the operation code and these are followed by two four-digit addresses (memory locations).

The code has the symbolic form

θ	$\hat{A}$	$\hat{B}$

where

θ = operation code, two digits
$\hat{A}$ $\hat{B}$ = address, four digits each

Table 1 lists several operation codes and their description. Q and Q' refer to numbers in the accumulator after the operation has been performed. This number is retained for additional operations or may be sent to the memory. If address zero is specified in the instruction word, the operation is performed on the number in the accumulator.

Table 1

Operation code	Operation	Description
50	Add	$A + B \rightarrow Q$
51	Subtract	$A - B \rightarrow Q$
52	Multiply	$A \times B \rightarrow Q$
53	Divide	$A \div B \rightarrow Q$
56	Addiply	$Q + A \times B \rightarrow Q'$
57	Subtiply	$Q - A \times B \rightarrow Q'$
64	Compare	if $A < \|Q\|$, take next instruction from $\hat{B}$.
65	Move or store	$A \rightarrow B, Q$
73	Read in (To memory)	Read in from paper tape and then take next instruction from $\hat{B}$.
74	Read out (Of memory)	Read out $\hat{A}$ words from consecutive locations starting at $\hat{B}$.
75	Stop	

In a similar manner the numerical data on which the computer shall operate must be presented in a coded form. For a problem such as the present one, in which the data and the results cover a range of magnitudes greater than the number of decimal places available in a number word, a floating decimal is used. Numbers are expressed in the familiar exponential form. The first digit of the code is used as the sign digit, the next two digits hold the exponent, and the final eight digits hold the numerical part, i.e., the *number words*, or data, have the symbolic form

$\pm$	X	A'

where $1 \leq A' < 10$, and the actual value of the number $A = A' \times 10^{x-50}$. The number 50 is introduced into the code for the exponent in order to have a positive number represent a negative exponent. For example, suppose we have assigned the equilibrium constant K_6 at address 26 in the memory. We would represent the data as follows:

Address	Sign	Exponent	Number→		Notation
0026	+	43	1590	0000	K_6

$K_6 = +1.590 \times 10^{-7}$ i.e. +4315900000

Example: Evaluate

$$E = \left[\frac{AB + C}{D}\right]^2$$

and store the result in address 150. Assume the number words A, B, . . . are stored beginning at address 100 and that instruction words are stored sequentially at address 300. The first instruction word will tell the computer to add the two numbers in addresses 100 and 101. The program for this problem can be seen in Table 2:

Table 2

Address	θ	A	B	Notation→
0300	52	0100	0101	$A \times B \rightarrow Q_1$, $Q = AB$
0301	50	0000[a]	0102	$Q + C \rightarrow Q_1$, $Q_1 = AB + C$
0302	53	0000	0103	$Q_1/D \rightarrow Q_2$, $Q_2 = (AB + C)/D$
0303	52	0000	0000	$Q_2^2 \rightarrow Q_3$, $Q_3 = [(AB + C)/D]^2$
0304	65	0000	0150	$Q_3 \rightarrow 150$.
0305	75	0305	0000	STOP

[a] 0000 is the address of the accumulator.

Numerical Analysis and Programming

There are many ways to approach a problem of this type. In this case a successive approximation process was used which requires an initial guess for the answer. A logical approach would be to reduce the number of initial guesses required as the answers will vary by several orders of magnitude. As the problem stands now, 10 such guesses would be required. By simple substitution the number of equations and the number of unknowns may be reduced while at the same time the remaining equations are made more complex. This reduces the number of initial guesses that must be made. We chose to reduce the equations (1–10) by simple substitution until elimination of any more unknowns become awkward. By this method the ten equations were reduced in a straightforward manner to 3 equations and 3 unknowns.

Solving the 3 equations has an advantage over solving one equation because the programming is simpler. After the 3 answers are evaluated, they can be used in equations (1–10) to solve for all the remaining answers. Equations 11, 12, and 13 result from the reduction.

$$0 = -K_2K_8 + G(-K_8 + K_2 + K_8 + G) + H\left[K_8 + G\left(1 + \frac{2(K_8+G)}{K_9}\right)\right] \quad (11)$$

$$0 = -K_1H^2G + B\left[\frac{K_6}{K_{10}}G^2H + H^2G + \frac{K_{10}}{K_5}H^3 + \frac{K_7K_6}{K_{10}^2}G^3\right] \quad (12)$$

$$0 = G^2\left[\frac{K_6}{K_{10}}B + \frac{H^2}{K_9}\right] + GH(-K_4 + 2B + H) + H^2\left[K_{10} + \frac{3K_{10}B}{K_5}\right] \quad (13)$$

Algebraic formulas exist for the solutions of the general quadratic, cubic, and quartic equations. These formulas are often too laborious to apply to specific cases. A well-known successive approximation procedure for solving a set of equations such as these and quite suitable for programming on a digital computer is the Newton-Rapheson method (*3*). As an example, let us consider 2 equations and 2 unknowns.

$$f(x,y) = 0 \quad (14)$$
$$g(x,y) = 0 \quad (15)$$

Let (x_0, y_0) be initial approximate value of the roots. We are then interested in finding a correction on x_0 and y_0 which we will designate at Δx and Δy respectively. The true roots are:

$$x = x_0 + \Delta x \quad (16)$$
$$y = y_0 + \Delta y \quad (17)$$

We then have:

$$f(x_0 + \Delta x;\ y_0 + \Delta y) = 0 \quad (18)$$
$$g(x_0 + \Delta x;\ y_0 + \Delta y) = 0 \quad (19)$$

These equations may then be expanded by Taylor's theorem.

$$f(x_0 + \Delta x, y_0 + \Delta y) = f(x_0,y_0) + \frac{\partial f}{\partial x}\Big|_{x_0,y_0}\Delta x + \frac{\partial f}{\partial y}\Big|_{x_0,y_0}\Delta y + \ldots = 0 \quad (20)$$

$$g(x_0 + \Delta x, y_0 + \Delta y) = g(x_0,y_0) + \frac{\partial g}{\partial x}\Big|_{x_0,y_0}\Delta x + \frac{\partial g}{\partial y}\Big|_{x_0,y_0}\Delta y + \ldots = 0 \quad (21)$$

Ignoring all terms of order higher than the first, we are left with a system of 2 *linear* equation in two unknowns, namely, Δx and Δy.

$$\frac{\partial f}{\partial x}\Big|_{x_0,y_0}\Delta x + \frac{\partial f}{\partial y}\Big|_{x_0,y_0}\Delta y = -f(x_0,y_0)$$

$$\frac{\partial g}{\partial x}\Big|_{x_0,y_0}\Delta x + \frac{\partial g}{\partial y}\Big|_{x_0,y_0}\Delta y = -g(x_0,y_0)$$

After solving the above for Δx and Δy, the process is repeated:

$$x_1 = x_0 + \Delta x \quad (22)$$
$$y_1 = x_0 + \Delta y \quad (23)$$

We similarly evaluate the new functions and their partial derivatives at (x_1, y_1). This repetition is carried to the desired degree of accuracy. The Newton-Rapheson method can be expanded to handle any number of equations.

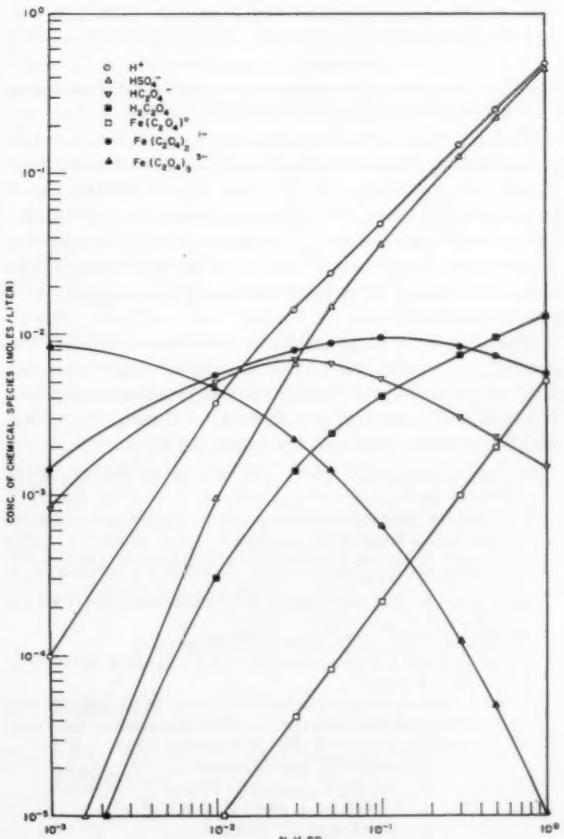

Figure 1. Effect of sulfuric acid concentration on the distribution of chemical species in 0.01 M ammonium tris-(oxalato)ferrate(III).

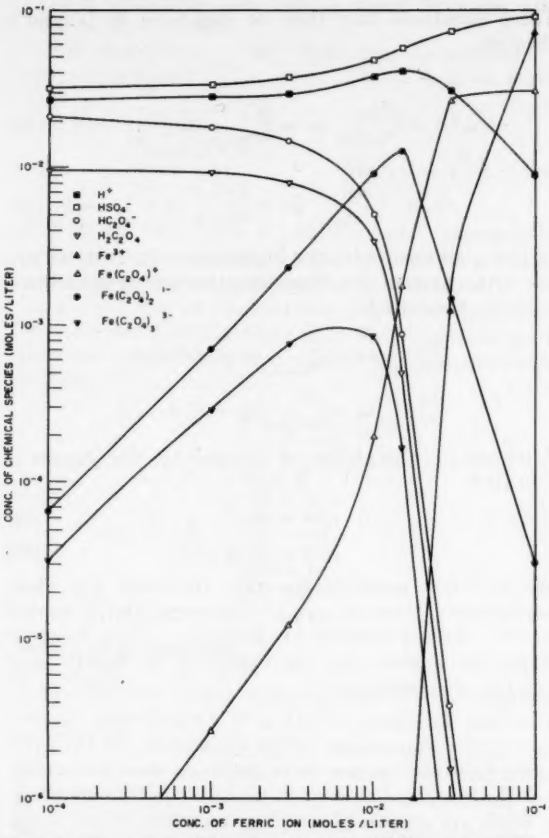

Figure 2. Concentration of the various species in 0.03 *M* potassium oxalate-0.1 *N* sulfuric acid on addition of ferric ammonium sulfate.

The procedure to be followed to put the present problem in a form for programming is now apparent. From our equations 11, 12, and 13 we obtain the 9 partial derivatives, 3 equations relating the delta values of the variables to the functions and their partial derivatives evaluated at the estimated values of the roots, and the 3 equations correcting the approximate root by the delta value.

The program of the problem then must instruct the computer to carry out the following with the 13 numbers to be fed in (6 values of the physical constants K_5 to K_{10}, 4 values of the material balance, K_1 to K_4, and 3 initial estimates of the roots H_0, G_0, and B_0):

(1) Evaluate equations 11, 12, and 13 when $H = H_0$, $G = G_0$, $B = B_0$.
(2) Evaluate the nine partial derivatives for the same values.
(3) Use the 12 numbers from steps 1 and 2, which are coefficients in the equations relating ΔB, ΔG, and ΔH, to solve for these corrections.
(4) Add ΔB to B_0, etc., to obtain new estimates of the roots B_1, G_1, and H_1.
(5) Obtain $\Delta B/B_1$, $\Delta G/G_1$, and $\Delta H/H_1$ and if
  (a) any one is greater than 10^{-6}, start again at step 1 with $H = H_1$ etc.
  (b) no one is greater than 10^{-6}, take these values of B, G, and H and solve for the remainder of the roots of equations 1–10 in the following order:
    1. from G, H, and (9) obtain I
    2. from G, H, and (10) obtain J
    3. from G, H, I, and (3) obtain F
    4. from F and (2) obtain E
    5. from B, J, and (5) obtain C
    6. from B, J, and (6) obtain A
    7. from A, J, and (7) obtain D
  (c) print out the values of A–J
  (d) stop

The complete program represented 250 steps. A portion of it as an example is presented in the following:

If we let F(H,B,G) represent equation (12), then the $\left.\frac{\partial F}{\partial B}\right|_{B^0,H^0,G^0}$ is one of the partial derivatives evaluated at estimated values of the variables. Equation (24) shown below results when $\partial F/\partial B$ is derived.

$$\frac{\partial F}{\partial B} = \frac{K_7K_6}{K_{10}^2}G^3 + \frac{K_6}{K_{10}}HG^2 + H^2G + \frac{K_{10}}{K_5}H^3 \qquad (24)$$

The programming of this equation (24) is shown in Table 3 in the form actually used. This part of the program starts at address 314. Previous addresses were used to solve equations 11, 12, and 13, and combinations of constants that are repeatedly used.

Table 3

Address	θ	$\hat{A}$	$\hat{B}$	Notation
314	52	0038	0038	H^2
315	65	0000	0078	Q_1 stored in 78
316	52	0000	0038	H^3
317	65	0000	0079	Q_2 stored in 79
318	52	0203	0037	$\frac{K_7K_6}{K_{10}^2}G$
319	56	0201	0038	$\frac{K_7K_6}{K_{10}}G + \frac{K_6}{K_{10}}H$
320	52	0000	0037	$\frac{K_7K_6}{K_{10}^2}G^2 + \frac{K_6}{K_{10}}HG$
321	50	0000	0078	$\frac{K_7K_6}{K_{10}^2}G^2 + \frac{K_6}{K_{10}}HG + H^2$
322	52	0000	0037	$\frac{K_7K_6}{K_{10}^2}G^3 + \frac{K_6}{K_{10}}HG^2 + H^2G$
323	56	0202	0079	$\frac{K_7K_6}{K_{10}^2}G^3 + \frac{K_6}{K_{10}}HG^2 + H^2G + \frac{K_{10}}{K_5}H^3$
324	65	0000	0007	Q_3 stored in 7

The entities at addresses 203, 201, and 202 are terms which were solved earlier and stored. They are respectively K_7K_6/K_{10}^2, K_6/K_{10}, and K_{10}/K_5. Let us examine step 319 more closely. In words, we have accomplished the following: Take the number at address 318 [(K_7K_6/K_{10}^2) G] and perform an addiply, that is, multiply the number at address 201 (K_6/K_{10}) by the number at address 38 (H) and then add this product to (K_7K_6/K_{10}^2) G.

Solving the Problem

In the above manner the entire problem is programmed and "read in." This includes all instructions and numerical data $K_5 - K_{10}$. In order to obtain answers, we need only to supply 7 additional numerical values. Take as an example problem a 0.01 *M* solution of $Fe(NH_4)_3(C_2O_4)_3$–0.001 *N* in H_2SO_4. Four of the necessary values (K_1 to K_4) can be immediately written down:

$K_1 = Fe_T = 0.01\ M$, in code, 4810000000
$K_4 = (C_2O_4)_T = 0.03\ M$, in code, 4830000000
$K_2 = (SO_4)_T = 0.0005\ M$, in code, 4650000000
$K_3 = (H)_T = 0.001\ N$, in code, 4710000000
(where T refers to total amount)

The 3 remaining entities are the initial guesses for $[H^+](G_0)$, $[HC_2O_4^-](H_0)$, and $[Fe(C_2O_4)_2^-]$ (B_0).

These 7 coded values are then "read in" and the computer is instructed to start the calculations. Depending on the number of iterations the machine performs (this in turn depends on the values assigned for the initial guess) the time required to solve the problem varied from 1–10 min. Several tris-(oxalato)-ferrate(III) solutions in varying sulfuric acid concentrations were analyzed on the computer, and the results are presented graphically in Figures 1 and 2.

Once a problem of this kind has been programmed and coded it may be used to solve for the concentrations of ions in other equilibria of the same type. This one has been used for the ferric oxalate-oxalic acid-perchloric acid system by simply assigning the value 1000 to K_3, representing complete dissociation of the acid.

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A Simplified Apparatus for Pressure Reactions

The conventional Carius combustion tube, used for performing small scale organic reactions under pressure in the laboratory, has been modified in order to make it more adaptable for routine use. For most laboratory workers it is difficult to produce a proper heat seal of the Carius tube; tubes often burst below rated pressure because of residual strains in the glass seal. Gordon[1] described an improved type of combustion tube made by sealing a smaller diameter tube on the heavy-walled tube; in this way all the seals except the small final seal can be oven-annealed at the factory. The disadvantages of the latter tube are: (1) the greater difficulty in filling, especially if any solids are involved, and (2) the still present problem of properly sealing the smaller opening.

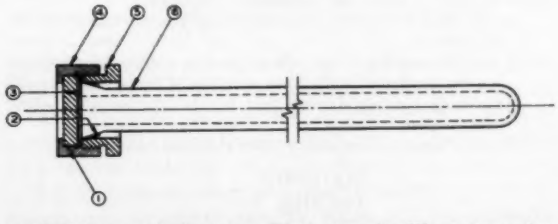
The modification described in this paper contributes to easier operation and greater economy over previously described equipment. No glass blowing experience is necessary and the same tube can be used repeatedly. The assembled combustion tube consists of an 18-in. length of flanged Pyrex pipe[2] of $^1/_2$-in. i.d. permanently sealed at one end and capped at the other end with a suitable gasket, aluminum disc, and aluminum screw cap[3] as shown in the accompanying illustration. The total volume of the pressure tube is 53 ml, thus permitting reactions of a total volume of about 35 ml to be performed. A Teflon gasket can be conveniently made and is suitable for most types of reactions. Other gasket materials may be employed. The pressure vessel can be heated, if desired, by placing it in an appropriate length of 2-in. steel pipe sealed at both ends by steel screw caps and placing the complete unit in an oven at any desired temperature.

Because of its construction the modified pressure tube is a substantial improvement over the conventional type. It affords a superior type of seal with greater strength at the point of closure than at any other part of the tube. This is in direct contrast to the ordinary type of Carius combustion tube which is weakest at its seal point. According to Gordon[1] the conventional Carius combustion tube will stand pressures up to 1500 lb per sq in. at temperatures up to 300° whereas his modified tube will stand pressures of more than 2500 lb per sq in. The reusable pressure tube described in this article can be expected to be as resistant to reaction pressures as Gordon's tube.

Reactions which have been run successfully in this apparatus are the following: (1) Inversion of sucrose at 149°C in dilute HCl. (2) Preparation of 5-hydroxymethylfurfural from sucrose and oxalic acid at 162°C in aqueous solution. (3) Preparation of diethyl aspartate and 2,5-diketopiperazinediacetamide from diethyl maleate and alcoholic ammonia at 105°C.

These are only a few examples of the flexibility of this reactor for conveniently carrying out small-scale pressure reactions. If a larger volume is desired, a tube of longer length and/or larger diameter can be used.

Tubes made of Pyroceram, a new Corning glass product reportedly harder than steel and light as aluminum, should extend the scope of this technique. Larger scale pressure reactions will be possible because of the greater wall strength of this material.



Modified Carius combustion tube. (1) Alumiuum disc, (2) asbestos gasket, (3) Teflon gasket, (4) aluminum screw cap, (5) aluminum ring, (6) flanged $^1/_2$-in. id Pyrex pipe.

[1] GORDON, C. L., *J. Research Natl. Bur. Standards*, 30, 107 (1943).
[2] Manufactured by Fischer and Porter Company, Hatboro, Pennsylvania.
[3] Screw cap assembly available from Fischer and Porter Company as standard equipment.

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Two Student Experiments on Chemical Equilibrium

The conventional laboratory course in physical chemistry includes and may even consist exclusively of a sequence of carefully documented experiments. Unless the documentation *is* rather detailed, the experiment is likely to be very time-consuming or to lead to results regrettably divergent from theoretical expectation. There is little room for Cortez or wild surmise in such a sequence and accordingly the interspersion of an occasional experimental "problem" or "practical examination" can be a welcome challenge to the student. My own practice is to give two or three such examinations in the course of two terms of physical chemistry. Every student works independently during the examination and is expected to present a written report on his work at the end of three or four hours.

A description follows of two of the experimental problems that I have used for such examinations. The first of these, on the ammonia silver complex, was a part of the Oxford University final A.B. examination in 1924; the second, a reconstruction of the classical work of Nernst on the solubility product, is (like the first) included in somewhat different form in "Problems of Practical Physical Chemistry" by the late F. A. Philbrick (J. M. Dent, London, **1931**) a useful little book now unfortunately out of print.

The Establishment of the Formula of a Complex Ion

The instructions given to each student are as follows:

Add to 20 ml of $M/100$ silver nitrate solution 10, 20, and 30 ml of 2 M ammonia solution. Make up each solution up to 100 ml with distilled water and then find what volume of $M/100$ KBr solution is necessary to produce a permanent cloud of silver bromide.

Basing your procedure on the results obtained, carry out a second series of experiments, arranging the volumes of each liquid taken so that the *total* volume of solution (including the added KBr solution) is always approximately 100 ml. This second series should cover at least a threefold range of ammonia concentration. For the second series, plot the log of the volume of KBr solution required against the log of the volume of ammonia solution used.

From your results deduce the probable formula of the complex cation formed by silver and ammonia. Note that

Ammonia solution can be treated simply as a solution of NH_3 in water;

It may be assumed that in the presence of any appreciable excess of ammonia the concentration of free silver ions will be small compared with that of the ammoniated silver complexion;

For *any* solution containing silver ions and ammonia

$$\frac{[Ag^+][NH_3]^n}{[Ag(NH_3)_n{}^+]} = K_1$$

and at the point where the precipitate *just* forms

$$[Ag^+][Br^-] = K_2$$

The volumes of solution required by each student are on a generous basis as follows:

0.01 M $AgNO_3$	150 ml
0.01 M KBr	150 ml
2 M NH_3	150 ml

The success of the experiment is quite insensitive to deviations of the solutions from their nominal concentrations, although students should be warned against leaving ammonia solutions unstoppered. A buret, 10-ml pipet, 50-ml graduate, and a couple of Erlenmeyer flasks are the only equipment needed. It is my custom with this experiment to allow two and a half hours for experimental work and to ask for a written report on the experiment at the end of three hours; this allowance of time is entirely adequate for the average student.

A student of unusual aptitude, after completing the experiment described above, can be invited to try similar experiments with ammonium thiocyanate instead of potassium bromide and to infer from them the ratio of the solubility products of silver bromide and silver thiocyanate. This, unlike the main experiment, is rather difficult as the precipitation point with thiocyanate is notably less sharp than with bromide. Even with potassium bromide as precipitating agent the room for difference of opinion as to what is a "permanent cloud" usually causes unnecessary preliminary distress among those who are reluctant to reflect on the purpose of the measurements and who prefer sure-fire culinary instructions.

This experiment using simple solutions and apparatus is successful in the hands of the great majority of students. Some may need assistance in the interpretation of their experimental results (and are downgraded accordingly) but it is quite rare to get results which, appropriately analyzed, do not lead to the correct formula for the complex ion.

EDITOR'S NOTE: Our usual policy is to ask authors of papers describing experiments to include sample calculations or typical student results.

Since we know that students do read the JOURNAL OF CHEMICAL EDUCATION, and we hope that professors will constantly encourage them to do so, both the author and the editor agree that publishing typical results would spoil the effectiveness of the present article. Such information is available to those who will communicate directly with the author.

It is one of the joys of the editor's life to be able to publish articles which stimulate ingenuity. We hope that those who adopt the procedures here suggested will devise similar experiments and share them with others through the pages of THIS JOURNAL.

The Solubility Product of Silver Acetate

This experiment, which involves a good deal more work in the preparation of solutions beforehand, is more exacting and more discriminating than the one just described. It requires about fifteen minutes of laboratory work on one day, followed (not *less* than 24 hours later) by a main laboratory period of two and a half to three hours.

The instructions given to each student are as follows:

The principle of the solubility product was put forward by Nernst in a paper two years after the first enunciation of the theory of electrolytic dissociation by Arrhenius. Seldom has a principle of such extended usefulness been put forward on the basis of more limited experimental evidence; it is also probably fair to say that few principles of a quantitative character have been accepted on the basis of such a sketchy accord with theoretical predictions.

The experiment to be carried out is essentially a reconstruction of the experiments carried out by Nernst in 1889, (*Zeit. phys. Chem.* **4**, p. 372, 1889).

You are provided with the following solutions:

A saturated solution of silver acetate in water
A saturated solution of silver acetate in 0.2 *M* potassium nitrate
1.10 *M* silver nitrate solution
1.10 *M* sodium acetate solution
5% potassium chromate solution
0.0500 *M* potassium chloride solution

(a) To 100 ml of saturated silver acetate solution in water (which need not be free from suspended solid and can be measured with a graduated cylinder) contained in a 250 ml Erlenmeyer flask add 10 ml of the silver nitrate solution and cork the flask.

(b) Treat a similar volume of saturated silver acetate solution with 10 ml of the sodium acetate solution in the same way.

(c) Leave both solutions to stand overnight in a cupboard, giving them an occasional swirl to mix up the contents without allowing the solution to come into contact with the cork.

(d) *On the following day (or later)*, pipet 25 ml of the potassium chloride solution into a 125-ml Erlenmeyer and add about 1 ml of potassium chromate solution. Titrate this solution with the *filtered* saturated solution of silver acetate by "Mohr's method;" the end-point is marked by the appearance of enough silver chromate to change the bright pale lemon color of the mixture to rather dirty yellow. This precipitation titration should be carried out at least twice to enable you to formulate your own convention as to the end-point. The dodge of holding back about 5% of the solution to be titrated until the end-point has been reached with the main batch will eliminate wastage of time in creeping up on the end-point of this and all other titrations in the experiment.

(e) In a similar way titrate 50 ml of potassium chloride (plus about 2 ml of potassium chromate solution) with the *filtered* solution of silver acetate containing silver nitrate. A duplicate titration of this is not necessary unless you feel uncertain about the first end-point.

(f) In a similar way titrate 25 ml of potassium chloride solution (plus about 1 ml of potassium chromate solution) with the filtered solution of silver acetate containing sodium acetate.

(g) From the results of (d) calculate the concentration (in gram-ions per liter) of silver in the saturated solution of silver acetate in water and hence the solubility product of silver acetate.

(h) From the result of (e) calculate the concentration of silver ion in the saturated solution of silver acetate containing 0.10 *M* silver nitrate. The concentration of acetate ion present in the solution is obtained by *deducting* 0.10 from the result obtained. Hence calculate the solubility product for this solution.

(i) From the results of (f) calculate the concentration of silver ion in the saturated solution of silver acetate containing 0.10 *M* sodium acetate. The concentration of acetate ion present in the solution is obtained by *adding* 0.10 to the results obtained. Hence calculate the solubility product for this solution.

(j) Draw up a table for the results of your calculations in the following form:

	$[Ag^+]$	$[Cl^-]$	$[Ag^+] \times [Cl^-]$
Silver acetate alone			
Silver acetate and silver nitrate			
Silver acetate and sodium acetate			

(k) Examine the constancy (or inconstancy) of the three values of the solubility product and reconsider the matter after titrating 25 ml of the potassium chloride (plus about 1 ml of potassium chromate solution) with a *filtered* saturated solution of silver acetate in water containing 0.2 *M* potassium nitrate solution. The silver ion concentration of this solution and the solubility product derived from it should be added to the table constructed under (j).

Notes

A graduate cylinder, used carefully, is sufficiently accurate for measuring the 100 ml portions in (a) and (b); all other measurements should be made with pipets; the volume of potassium chromate solution need not be measured to closer than 10%.

Less than 50 ml of filtered solutions will be required in the titrations of (d), (e), (f), and (k) so there is no need to filter more than this volume from the turbid solutions concerned.

Each student needs 150 ml of 0.0500 *M* potassium chloride solution, 300 ml of saturated silver acetate solution, 50 ml of 0.2 *M* potassium nitrate solution saturated with silver acetate, 20 ml of each of 1.10 *M* silver nitrate and 1.10 *M* sodium acetate, and 10 ml of 5% potassium chromate solution. In the interests of economy the volume of silver acetate solution needed can be halved by carrying out experiments (a) and (b) on half the scale prescribed, although this is cutting it a little fine; the cost of silver salts on the scale recommended is around 35 cents per student.

In preparing the solutions required for the experiment it should be noted that only the solutions of 0.05 potassium chloride and of 1.10 *M* silver nitrate call for accurate weighing in their preparation. With regard to the saturated solutions of silver acetate in pure water and in 0.2 *M* potassium nitrate respectively, it should be noted that the saturation equilibrium is established rather slowly (from the un-saturated side) so that it is wise to make up these solutions *at least* three days before the experiment is to be carried out. This is particularly desirable if in the interests of economy it is planned to use a limited excess of the relatively expensive solid phase.

Four liters of the saturated solution of silver acetate in water are conveniently prepared by dissolving separately 72 grams of silver nitrate and 60 grams of sodium acetate trihydrate in two 125-ml portions of distilled water. The two solutions are mixed and the precipitated silver acetate is separated on a Buchner funnel. The precipitate is washed with about half a dozen portions of distilled water, totalling 300–400 ml. The washed precipitate is then transferred to a four-liter container (preferably of dark glass) which is then filled with 4 liters of hot distilled water. This storage vessel should be shaken (and warmed, if possible) from time to time during the next three or four days. In preparing on a smaller scale the corresponding saturated solution in 0.2 *M* potassium nitrate, the distilled water is replaced by potassium nitrate solution. For obvious reasons, the solutions in which solubility equilibrium is being established should be protected from violent

temperature fluctuations. A laboratory cupboard is adequate for this purpose; the thermal history of all the solutions should be similar. Although adequate time (3–4 days) is needed to establish equilibrium in the original saturated solutions in water and in 0.2 *M* potassium nitrate, it is *not* desirable to prepare such solutions months beforehand as progressive change in concentration (presumably due to growth of crystal size) may cause anomalous results.

Whereas the experimental results of the silver ammonia complex experiment may startle some students by their conformity with theoretical expectation, exactly the opposite situation prevails in the case of the solubility of silver acetate. The student will find that the solubility product (expressed in concentration units) is not constant and that its deviations from constancy are outside any expected experimental error. The average student is likely to find this distressing and, although it would be unfortunate to do this at the outset, he may then be shown a copy of Nernst's own experimental results after he has completed part (j). Experiment (k) then allows the better students an opportunity to surmise the reason for the inconstancy of the solubility product and to acquire a deeper understanding of the situation than Nernst himself had at the time of his original paper.[1]

Of the two experiments described the first is easier to set up, is less demanding in the way of chemicals and apparatus, and is less rugged on the student. Both were carried out effectively by the participants in a Summer Institute for high school teachers organized at Princeton University in 1958 by Professor Clark Bricker with the support of the Dreyfus Foundation. Many other experimental problems can be devised and some would doubtless be more effective than those described here. The essential purpose of this paper is to urge the value and stimulus of putting the student, working alone, in a moderately unfamiliar experimental situation with no more guidance and instruction than may be needed to give him a sporting chance of solving the problem presented to him. The student will have to think harder than in carrying out experiments with rather elaborate instructions; the heartening fact is that he often seems to enjoy the more adventurous situation.

[1] Such students might well be interested by RAMETTE, R. W., J. CHEM. EDUC., **36**, 191 (1959), and DAVIES, P. B., and MONK, C. B., *J. Chem. Soc.*, **1951**, 2718.

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A Half-Life Experiment for General Chemistry Students

The need for including nuclear chemistry experiments in the first year course, especially for the nonscience major, is well recognized, and several good experiments have been described in the chemical literature. Among these, the measurement of the half life of an unstable isotope has received considerable attention.[1] This paper is to describe our experiences over the past two years with the measurement of the half life of bismuth-210 by large numbers of first year students. The choice of this isotope[2] is predicated upon several favorable factors.

(1) The bismuth is continually supplied from cheap radiolead ($^{210}_{82}$Pb, $t_{1/2}$ = 22 years) obtained from uranium minerals so that once a supply is obtained, it lasts for several years. Further, after the solutions have been prepared for the first time and the apparatus accumulated, little additional work is required on the part of the storeroom personnel to ready the exercise for the next quarter's or the next year's classes.

(2) The half life is short (5.0 days) so that the rapid fall in activity permits the use of cheap rate-meters, yet it is not so short as to require undue haste in handling; moreover, since each student counts his sample only once during a laboratory period for three successive laboratory meetings, the number of counters needed to serve a given number of students is at a minimum. We find one counter is adequate for a section of 40 students.

(3) The stock solutions are not hot enough to require shielding, yet the 1.17-Mev beta radiation is sufficiently energetic to require no special counting techniques. The daughter isotope, $^{210}_{84}$Po, is relatively long-lived and emits alpha radiation which is stopped by a scotch tape, the granddaughter is stable lead-206. Consequently, only the beta radiation emanating from bismuth-210 is counted.

(4) The fact that the starting material and the decay products represent a segment of the well-known uranium-238 series of radioactive elements adds interest to the work and serves to better correlate the laboratory work with lecture work.

[1] BROWN, CHARLES A., AND ROCHOW, E. G., J. CHEM. EDUC., **28**, 521 (1951); DILLARD, CLYDE R., AND MORTON, LYNWOOD, J. CHEM. EDUC., **35**, 238 (1958).

[2] We are indebted to Dr. G. K. Schweitzer of the University of Tennessee for recommending this isotope.

The Experiment

The student removes a 10-ml sample of radiobismuth chloride from the stock solution and uses this sample to

plate out on a $^1/_4 \times {}^1/_2$-in. piece of nickel-foil enough bismuth to give the desired initial count, about 1200 counts per minute. Since bismuth is below nickel in activity, the plating occurs spontaneously:

$$3Ni + 2BiCl_3 \rightarrow 3NiCl_2 + 2Bi$$

The parent isotope, lead-210, does not plate on the nickel foil. About 25 minutes at room temperature or

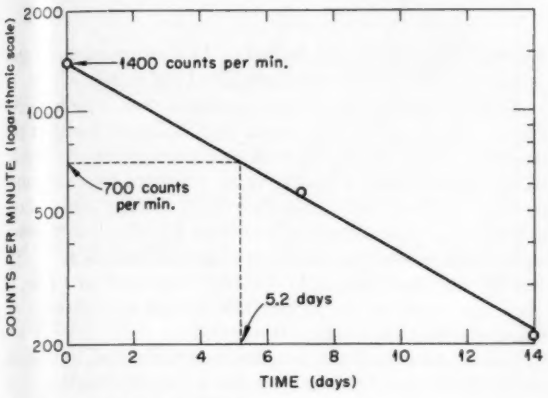

Figure 1. Typical student graph.

3 minutes at 100°C are required for the plating. The solution is then returned to the stock bottle.

The nickel foil with the radiobismuth is now fastened to a copper planchet by means of scotch tape. The sample is then counted by the student at each successive laboratory meeting for a period of 14 days. These data are plotted on semi-log graph paper and the half life is read from the graph.

Figure 1 shows a typical student graph. Table 1 shows the results obtained by 849 students during the spring of 1959. These are average students from the colleges of home economics, engineering, agriculture, business administration, education, law, and liberal arts (we do not permit our B.S. in chemistry majors to do this experiment since they will do similar ones later on at a more advanced level). The students were mainly under the supervision of teaching assistants, of whom only about two-thirds had had previous experience with nuclear chemistry experiments. Also, the staff was unaware of our intentions to collect the results.

Excluding the cost of the counter, we estimate that the experiment is costing from 2–4¢ per student. This low cost is due to the fact that the radioactive material, copper planchet, and nickel foil are reusable for several years. The cost of the counters is hard to estimate for we do not know how long they will last. Our three counters have survived two years of use (a total of 144 working hours for each) without a breakdown. Since about 2000 students have now done this experiment, the counter cost per student to date is 30 cents.

Table 1. Observed Half-Life[a] of $^{210}_{83}Bi$

No. of students	Half-life range
2	3.5 days or less
67	3.6–4.5 days
363	4.6–5.5 days
287	5.6–6.5 days
130	6.6 days or longer

[a] Accepted half-life—5.0 days.

The radiolead nitrate is added with stirring to 0.5 *N* HCl (one-fourth pound to 4 liters).[3] Most of the lead accumulates in the bottom of the bottle as $PbCl_2$. In our laboratories we place the supernatant liquid at convenient locations along with a 10-ml syringe pipet standing in a large graduated cylinder (to collect drainage). Each student removes his 10-ml sample and places it in a small beaker. After the plating has been accomplished, he returns the solution to the original stock bottle. These "spent" solutions are collected and returned to the bottle containing the $PbCl_2$. Since $^{210}_{83}Pb$ disintegrates to form $^{210}_{83}Bi$, the concentration of the bismuth will increase until "equilibrium" is again reestablished in the stock solution, a process which requires a few weeks. Hence, the stock solutions may be used several years if the radiolead is carefully husbanded. Since the $BiCl_3$ tends to become entrapped in $PbCl_2$ crystals where it forms, we have found it desirable to warm the stock mixture until the solid phase is dissolved and then cool to reprecipitate the $PbCl_2$. This is done the day before the supernatant liquid is to be removed for dispensing.

Several commercial makes of cheaper rate meters are

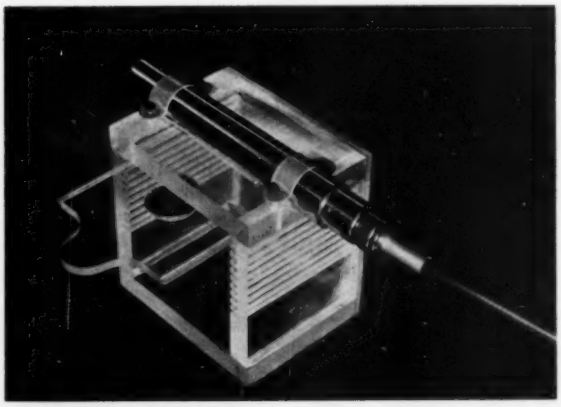

Figure 2. Counting chamber.

satisfactory for the counting. (We use Model 1613A Classmaster, Nuclear-Chicago.) Since these instruments usually are not equipped with counting chambers, it is necessary to construct a chamber such as the one seen in Figure 2. The Geiger tube is securely strapped to the frame so that it will not be moved with respect to the counting slots during the 2-wk counting period. The frame is constructed of wood, plastic, or metal. Also, the frame is built so that the sliding tray containing the sample may be placed very close to the Geiger tube. One or two of the metal guards protecting the Geiger tube are clipped out so that only air will be between the sample and the tube. This reduces the amount of bismuth that must be present to give a desired count. The sliding tray has a 1-in. circular depression in the center for positioning the copper planchet immediately underneath the window. The student, of course, must mark the planchet so that he can orient his sample with respect to the window in the same manner for each reading.

[3] Canadian Radium and Uranium Corp., 630 Fifth Avenue, New York. Minimum purchase, one-fourth pound ($12.50).

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Determination of Vapor Pressure

A general chemistry laboratory experiment

Laboratory manuals for the general chemistry course generally neglect a study of the properties of liquids. Most textbooks include vapor pressure–temperature curves for a few liquids. However, determination of such curves seldom is assigned to students, presumably because more than ordinary equipment is required to achieve accurate results. We are suggesting a method for obtaining good vapor pressure-temperature curves with equipment available in any general college chemistry laboratory.

For some years we have demonstrated the determination of a vapor pressure-temperature curve by any of a variety of simple methods (*1–5*). In our experience good results are not usually obtained by these procedures. Methods involving more elaborate equipment were also investigated (*6–10*). However, these make use of materials not generally available to students in general college chemistry.

The method of Devor looked attractive for a student experiment but requires a special type manometer not usually available. However, we did try this method but modified it by attaching the side arm of a suction flask directly to one end of a manometer after filling the flask with the liquid vapor and recording the pressures as the liquid cooled. After several trials this method

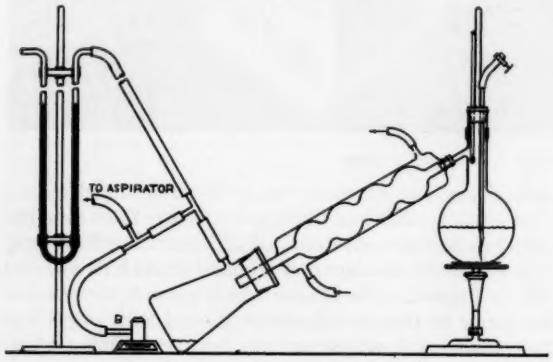

Figure 1.

was abandoned because too much time was required for the attainment of equilibrium between the liquid and its vapor, particularly at low pressures and temperatures.

A reflux method was also tried. For this purpose a two-neck flask containing the liquid was fitted with a thermometer and a condenser connected at its top to a manometer and an aspirator. This method was found to have the disadvantage that the reflux condenser flooded when the liquid boiled. As a consequence, the pressure and temperature fluctuated too much.

The final choice was to use a simple distillation technique. Although it may seem that a simple distillation under a variety of pressures should present no problems, it was found that a good vapor pressure-temperature curve is obtained only under certain carefully controlled conditions. Bumping was a problem in the lower pressure range, even when boiling stones were added. By far the best preventive is the old technique of using a very fine capillary to permit circulation of a stream of small air bubbles through the liquid.

Establishment of true equilibrium between liquid and vapor is absolutely necessary for accurate results. At first our practice was to begin distillation at atmospheric pressure and gradually to reduce to lower pressures. Such a procedure was found to give erratic results, particularly at the lowest pressures. Apparently this is due to the fact that, after the liquid has been heated enough to boil at the higher pressure, a lowering of the pressure requires the dissipation of considerable heat energy through evaporation of the liquid before a new point of equilibrium is reached at the lower temperature. It was found that it is far better to begin the distillation at the lowest pressure. Thereafter the pressure is increased to a definite value and just enough heat is applied to the liquid to make it distill at a predetermined rate, at which time the pressure and the maximum boiling temperature are read. In this way the liquid never possesses more heat energy than is necessary to make it boil, and better control is obtained.

The apparatus required is shown in Figure 1. It consists of an ordinary distillation unit. The 500-ml. distillation flask, equipped with a thermometer and a fine capillary to prevent bumping, is attached to a bulb-type condenser and receiving flask, and the latter to the manometer and pump. The whole system is evacuated by means of an aspirator rather than a vacuum pump to avoid traps needed to protect the pump from condensed vapors. The pressure is controlled by a bleeder valve, *B*. A screw-type Bunsen burner base works very well.

The Experiment

Put 250 ml of pure liquid in the flask and evacuate the system to the lowest possible pressure with valve *B* shut tightly. When the liquid starts to boil, open *B* a little to raise the pressure just enough to stop the boiling. Then heat the flask with a very small flame until the liquid again boils and distills at the rate of one drop per second. As soon as the temperature and pressure are stabilized at this distillation rate, read and record them. Now raise the pressure about 30 mm, apply a little more heat until the liquid again distills at a constant temperature and pressure and at the same rate as before, and again record the new values. It is important not to touch the valve, *B*, during this time. The only control required is the amount of heat which is applied to maintain a constant rate of distillation. Repeat as many times as desired to cover the whole range of pressures.

This paper reports another in a series of quantitative laboratory experiments for the general chemistry course developed originally as freshman research projects (see J. Chem. Educ., **34**, 133 (1957); **35**, 412 (1958). Work here reported was performed by Mr. Brummel and Mr. Vanden Bout during their freshman year at Calvin College.

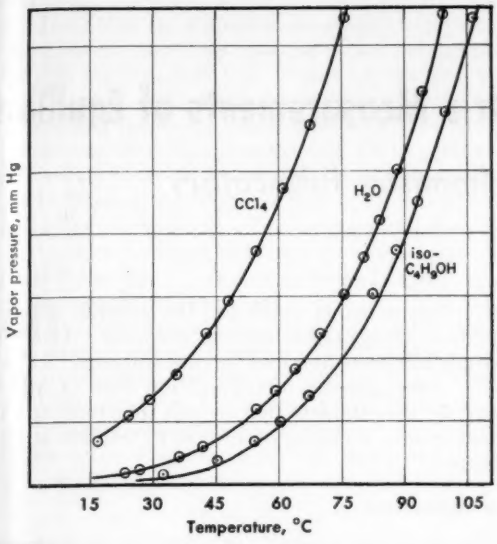

Figure 2.

Record the atmospheric pressure, and subtract all pressure values from it to get the actual pressures on the liquid for the various boiling temperatures. Plot these vapor pressure values against the temperatures to obtain the VP-T curve.

Student Results

Data were determined for three liquids: water, carbon tetrachloride, and isobutanol. In order to show the accuracy obtained by the students, Figure 2 gives the curves drawn from literature data and the actual experimental values (circles) obtained by the foregoing procedure. Students working in pairs can determine the data for two liquids in a three-hour period.

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Hollow Lantern Slides Illustrating Crystal Structure

The structure of simple crystals can be studied with the aid of models made from steel balls but these models are generally too small to be useful for classroom instruction. However, the effects observable in a single layer of such a crystal model can be shown to large classes by enclosing a layer of bearing balls in a hollow $3^1/_4$-in. by 4-in. lantern slide and projecting the shadow pattern.

The simplest situation, spheres of a single size free to move in two directions, is shown by means of slide *A* (Fig. 1). When the slide is horizontal the balls assume random positions; when it is tilted the balls simulate a single layer of polycrystalline material (Fig 2). Such features as the method of the closest packing of spheres, the regularity of crystalline areas and the nature of crystal boundaries, slip planes and holes in crystal lattices are apparent after one or two trials. Recrystallization and the looseness of atoms at crystal faces can be illustrated by tapping or vibrating the slide.

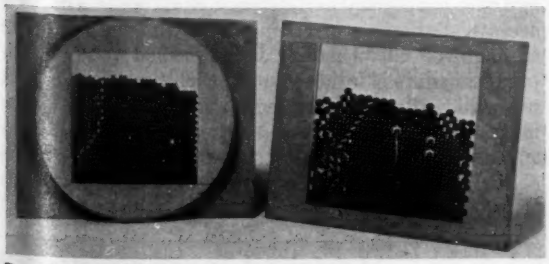

Figure 1. Slide *A* (left) and slide *B* (right).

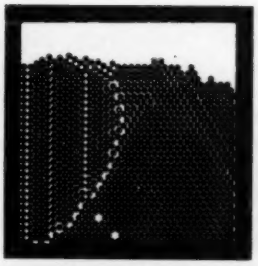

Figure 2. Shadow pattern of slide *A*.

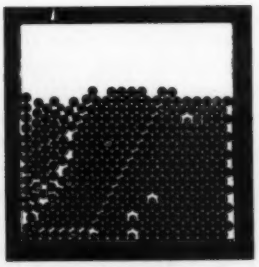

Figure 3. Shadow pattern of slide *B*.

Slide *B* (Fig. 1) shows the more complicated case in which a few smaller spheres (impurities) have been mixed with larger spheres. With this slide it can be shown (Fig. 3) that the smaller balls either accumulate at the crystal interface or occupy regular lattice sites (and thus create points of potential strain).

The slides were made from $^1/_{16}$-in. acetate sheet. Slide one contains about nine hundred $^1/_{16}$-in. steel bearing balls and slide two has about three hundred $^1/_8$-in. balls and a few $^3/_{32}$-in. balls.

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Potentiometric Measurements of Equilibria

In general chemistry laboratory

We describe in this paper an experiment in which the solubility product of silver chloride, the ionization constant of the silver-ammonia complex, and the ionization constant of acetic acid can be determined with one afternoon of work in the laboratory. Because the success of the experiment depends to a considerable degree on voltage measurement, we describe a student potentiometer which we designed and built for this particular exercise. Its cost is low enough—about $8—that most schools can afford one or more; its performance is excellent.

A similar experiment has been used at another university,[1] but vacuum tube voltmeters were used in that case for the voltage measurements. This limits greatly the accuracy possible and adds significantly to the cost of the experiment. We feel that the instrumentation we have developed is an important factor in the success of the experiment.

The experiment in question was developed for our college freshman course offered to students with good previous training in chemistry. We felt that before these students undertook qualitative or quantitative chemical procedures they should have a solid understanding of what ionization constants and solubility products are and how they are determined, and that while description and demonstration are both good, nothing could quite replace having the students do these determinations themselves. Accordingly, during the fall of 1958 we introduced a new group of experiments, all quantitative in character, which led by obvious stages to the determinations to which we have referred. These experiments laid a firm groundwork in use of the analytical balance, determinations of equivalent weights by several methods, establishment of the molar concept, use of titrations for determination both of millimolar quantities of materials and of concentrations. This last was followed by a titration determination of the solubility product of lead chloride using a silver-chloride titration with chromate end point. Following this, the equilibrium measurement of electromotive forces was developed both in lecture and laboratory discussion, with the specific experiment described in this paper. It is obvious that the necessary theoretical description and equations must be presented in advance and that the students must have had sufficient practice in manipulating figures if the experiments as a whole are to be meaningful. By working to this end and by insisting that the students learn theoretical and practical computing procedures as a part of the chemistry course, we feel we have overcome this difficulty. The term's laboratory closed with a lecture demonstration of the dynamic nature of equilibria using radiochemical examples. One such example has been described in THIS JOURNAL.[2]

The potentiometric determination was so well received by the students that we felt the procedures and potentiometer would be of interest to teachers at other schools.

The Experiment

The materials needed are: five 50-ml beakers, a graduate, a small U-tube to fit over two beakers, two corks and some scraps of filter paper to make the U-tube into a salt bridge, *p*H 7 buffer, 16 *F* ammonium hydroxide, 1.0 *F* potassium chloride, 0.10 *F* silver nitrate, 0.10 *F* acetic acid, and 0.10 *F* sodium acetate solutions, quinhydrone, two pieces of platinum wire, and one piece of silver wire to fit the beakers. Needed also is a suitable potentiometric apparatus for voltage measurement in the range 0.050 to 0.250 volt. The solutions were made by weight and volume measurement and were not standardized; they are probably correct to 1%. The *p*H 7 buffer was made from handbook directions for a sodium hydroxide-potassium dihydrogen phosphate buffer. Buffer tablets may be purchased to serve the same purpose.

The student prepares the salt bridge by filling the inverted U-tube with potassium chloride solution and stoppering it with the corks covered with strips of filter paper. He then makes three buffer solutions: 20 ml and 20 ml, 40 ml and 2 ml, and 2 ml and 40 ml respectively of sodium acetate and acetic acid; he carefully marks each beaker. In a fourth beaker he prepares a silver chloride precipitate from 1 ml of silver nitrate and 20 ml of potassium chloride. In the fifth beaker he procures some of the *p*H 7 buffer. All solutions are measured with the graduate; the graduate is rinsed between measurements with the solution to be measured next. A pinch of quinhydrone, about 0.1 g, is added to the four buffer mixtures sufficient to leave some solid after each has been stirred.

The voltage measurement is made in each case using the *p*H 7 buffer with platinum wire and the quinhydrone couple as the reference electrode. The three acetate buffers are compared with this reference through the salt bridge, which is washed in a little surplus potassium chloride solution each time it is changed, using the other platinum wire and quinhydrone as the measurement electrode. Next the silver chloride-silver wire couple is substituted and the voltage recorded. Finally 20 ml of 16 *F* ammonium hydroxide solution is added to the silver chloride precipitate;

[1] NASH, L. K., "The Chemistry 2 Workbook," Harvard University Printing Office, Cambridge, Mass., 1954.

[2] LIBBY, W. F., J. CHEM. EDUC., 34, 578 (1957).

the solution is stirred with the wire until the precipitate is dissolved; and the voltage measurement is repeated.[3]

The students were told that the potentiometer must be used in a methodical fashion just as they had been taught to weigh. One has to bracket the quantity to be measured and then approach it more and more closely, as closely as the potentiometer will allow. There is also the need to know the sign of the potential, which might be likened to knowing which is the left or right hand side of the balance. This analogy and their previous training in using the balance must have been successful for there were few questions or difficulties with the voltage measurement.

Students were given a mimeographed description of the exercise a week in advance of the experiment. The descriptive section on the computations elaborated upon the quinhydrone half-reaction and developed the measured potential differences in terms of the half-cells involved. The final result for the acetic acid buffer system was given as

$$\text{emf} = 0.059 \log [H^+]_{pos}/[H^+]_{neg}$$

where emf is the voltage read from the potentiometer, and $[H^+]_{pos}$ represents the concentration of hydronium ion at the electrode of designated sign. For the ionization of a weak acid like acetic acid,

$$HAcO \rightleftarrows H^+ + AcO^-; \qquad K_{HAcO} = [H^+][AcO^-]/[HAcO]$$

If AcO^- is added in the form of the salt, sodium acetate, to a solution of the acid, the final values of $[AcO^-]$ and [HAcO] will not differ significantly from the initial

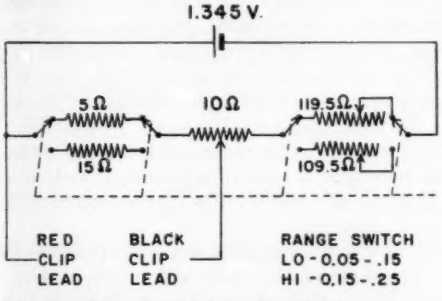

Figure 1. Circuit diagram for student potentiometer.

concentrations $[AcO^-]$ and [HAcO] and the potentiometric determination of $[H^+]$ allows computation of the equilibrium constant. Three such values are obtained, one for each buffer mixture.

In the case of the silver-silver chloride cell,

$$\text{emf} = E^0_{Ag} - E^0_{Qh} = -0.101 - 0.059 \log [Ag^+]/[H^+]$$

is appropriate if the cell reaction involves silver being oxidized, in which case the value of emf employed is positive. If the silver ion is reduced, the silver electrode will be positive, and a negative value of emf should be used in the expression. For the reaction

$$AgCl_s \rightleftarrows Ag^+ + Cl^-; \qquad K_{AgCl} = [Ag^+][Cl^-]$$

as used in this experiment, there will be a known $[Cl^-]$ of approximately 1 *M*, and the solution will be saturated with AgCl. The potentiometric determination of $[Ag^+]$ in equilibrium with these species will allow a calculation of K_{AgCl}.

[3] Be sure the silver ammonia complex is thoroughly washed down the drain after the experiment is completed as explosive residues are left on evaporation of the solution.

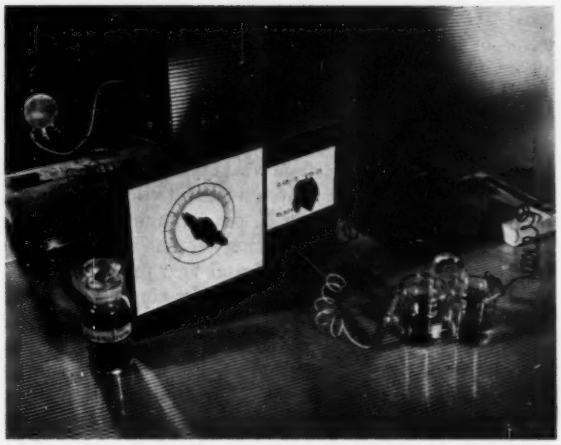

Figure 2. Photograph of student potentiometer and associated materials, equipment, and parts. The back of the potentiometer panel is reflected in a mirror, showing the Trim-pots, mercury cell, 10-ohm potentiometer, and range switch with wiring.

The Student Potentiometer

The circuit for the potentiometer is shown in Figure 1. It was constructed with a wood base and a Masonite panel using standard radio parts. A minimum of wood-working is involved. Figure 2 shows front and back views of the unit. The dial markings were drawn with ink on tracing paper, reproduced on Ozalid paper, and glued onto the panel with rubber cement. Holes for the shafts were cut in the paper with a sharpened cork borer. The finished product was sprayed with plastic transparent spray from an aerosol can to protect the labels. The parts list follows:

1—four-pole two-position tap switch such as Centralab Type PA-1011
1—10 ohm wire-wound potentiometer such as Centralab Series 58-10
1—2-in. Bakelite bar knob
1—mercury cell such as Mallory RM 12 R (3600 milliampere-hours)
1—5 ohm deposited carbon 1% resistor 1/2 watt
1—15 ohm deposited carbon 1% resistor 1/2 watt
2—200-ohm multi-turn wire-wound trimmer potentiometers such as Bourns Trimit Model 271
wire, sheet copper, brass screws, etc., as required

The basic requirement of the experiment is to measure voltages with the values 0.050 to 0.250 volt to at least one millivolt. An error of 1 millivolt will result in an error in calculated ion concentration of 4%. The potentiometer allows one to do this precisely with no difficulty. A total resistance of 134.5 ohms in series with a Mallory mercury dry cell sets a current drain of 10.00 milliamperes, since the voltage of the cell is a very stable 1.345 volts at room temperature. The cell used has a capacity of 3600 milliampere-hours so a life of well over 300 hours of actual use can be expected. The circuit divides the 134.5 ohms among selected end resistors and a 10-ohm potentiometer in such a way as to establish the 0.050- to 0.150- and 0.150- to 0.250-volt ranges. The actual values are given in Figure 1. Because one needs some adjustment to compensate for variation in the components, none of which is selected to better than 1%, and because the required upper resistance values are not stock sizes, we chose to use two Trim-pots to set the potentiometer current to the de-

sired 10.00 milliamperes. These are the most expensive items in the unit, but their use was felt justified since an ordinary potentiometer will not allow sufficiently fine adjustment when the potentiometer current is set.

After the units had been assembled, these two Trimpots were adjusted to give 0.0500 and 0.1500 volt with the potentiometer at its lowest position. The two-position switch chooses between these two voltages. A Leeds and Northrup Type K potentiometer was used for this measurement. Lacking it, one could utilize another Mallory mercury cell and two precision resistors as a voltage divider to obtain the common 0.1500-volt reading. Finally, the potentiometer shaft was set at the center voltage value, that is, 0.1000 or 0.2000 volt, and the knob tightened to point to the center mark on the handmade scale. To do this without the Type K or a similar reference potentiometer would require that another precision resistor be purchased to yield one of these voltages. In no case was the scale position found to be in error by more than a millivolt using this procedure for establishing the reading of the student potentiometer. Such errors as remained resulted from non-linearity of the potentiometer winding. These could be compensated for by calibration and would make the instrument useful to at least 0.1 millivolt within its narrow voltage range.

A galvanometer key was made (like the mercury cell holders) from sheet copper, cut, bent, and fastened to a wood block with brass screws. Oddly enough, the main thing to be careful about here is to burnish the copper strip and screws where contact is to be made and to *apply a modest touch of petroleum jelly* on these contacts. Evidently it is easier to squeeze away the coating of grease than to break through a semiconducting film of copper oxide or sulfide which is rapidly formed in the atmosphere of a laboratory. This apparently insignificant detail can well make the difference between success and failure of the experiment.

As a null-indicator we used box-type galvanometers borrowed from the physics department. Lacking this, one can use radio surplus microammeters successfully. The lower the current for full-scale reading, the better the precision of measurement.

Student Results

We have analyzed the results obtained by an arbitrarily selected sample of about 100 of the 300 students who did the determinations. The sample was picked at random from different laboratory sections on different days, but we cannot pretend to have made a careful statistical selection. Table 1 lists the results. The large number of determinations of the acetic acid ionization constant comes from the fact that each student does three such measurements. The term "acceptable determination" means within tenfold of the correct answer. The number of unacceptable determinations result almost entirely from errors in calculation. These calculation errors range from inability or failure to do the arithmetic correctly in the acetic acid case to inability to distinguish a mole from a molar solution in the silver-ammonia complex case. In almost all cases the recorded voltage measurements were correct. The most common error was failure by the student to recognize that when 10^{-4} mole of silver chloride is dissolved in a total volume of some 4l ml of solution on the addition of ammonia, the total silver concentration is not 10^{-4} molar.

Table 1. Average Results of Potentiometric Determinations

Equilibrium involved	$HC_2H_3O_2$	AgCl	$Ag(NH_3)_2^+$
No. of determinations	335	119	131
Acceptable determinations	297	86	45
Unacceptable determinations	38	33	86
Mean equilibrium constant computed from acceptable determinations	2.09×10^{-5}	2.49×10^{-10}	2.64×10^{-8}
Mean equilibrium constant corrected for ion activities	1.78×10^{-5}	1.51×10^{-10}	4.33×10^{-8}
Literature value of equilibrium constant at 25° C[4]	1.74×10^{-5}	1.56×10^{-10}	6.2×10^{-8}

When the results are averaged, the interesting conclusion is that the determinations are surprisingly close to the correct values.

One correction can be made, however, which makes the agreement even better. The literature values for the equilibrium constants are for infinite dilution; for the concentrated solutions used in this experiment, the literature values must be regarded as *activity* products. The cell potential measurements yield values for silver and hydrogen ion activities. In the calculations of the equilibrium constants, these activities were joined with the *concentrations* of chloride, acetate, and silver complex ions. If appropriate activity coefficients of 1.0 for neutral molecules, 0.85 for acetate ion, and 0.61 for chloride and silver complex ions are used,[5] the average values for $K_{HC_2H_3O_2}$ and K_{AgCl} are within 3% of the literature values. The mean complex ionization constant is probably in poorer agreement with the book value because of uncertainties in the actual NH_3 concentration and activity.

The ability to distinguish between activities and concentrations has pedagogical value. One can avoid mentioning the subject, and the students will accept the deviations as experimental error, or the instructor can furnish the student with the activity coefficients to enable him to compute corrected equilibrium constants.

The deviations from ideality show up in individual experiments as well as in the statistics of a large class. In one group of students the standard deviation of 17 determinations of the silver-chloride equilibrium constant was 8.6%. Thus the individual student can readily observe the application of the activity coefficients to the problem at hand.

We are currently working on the conditions for the use of thiosulfate instead of ammonia as a complexing agent for silver ion. The use of a dilute solution of thiosulfate gives promise of providing improved accuracy in the determination of a complex ion equilibrium constant.

[4] "Handbook of Chemistry and Physics," 35th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1637, 1635 1953; SIDGWICK, N. V., "The Chemical Elements and Their Compounds," Oxford, 1950, Vol. 1, p. 137.

[5] HARNED, H., AND OWEN, B. B., "Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Corp., New York, 1958, pp. 529, 727.

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Radiochemical experiments:

A Thorium 234 "Cow" for Pa-234

The only suitable tracers available for the study of the chemistry of thorium are the isotope 230, an α-emitter with an 80,000 year half life, which occurs in the U^{238} $(4n+2)$ decay series and Th^{234}, a β-emitter with a 24.1 day half life in the U^{238} $(4n+2)$ series. The recovery of Th^{230} from uranium purification wastes has been described elsewhere (*1*). It is the purpose of this paper to describe a method which has been found satisfactory for the isolation of Th^{234}. Its 24.1 day half life and the fact that it may be obtained from natural uranium compounds without neutron irradiation make this isotope suitable for college and university courses.

For half-life determinations, a half life of less than 10 minutes is desirable in order that an experiment may be completed in a single laboratory session. An isotope with such a short half life cannot be purchased and must be obtained from a medium- or long-lived parent. One suitable nuclide for half-life determinations is Pa^{234} which is the daughter of Th^{234}. The first members of the $4n+2$ radioactive series decay in the following manner:

$$U^{238} \xrightarrow[4.51 \times 10^9\ \text{yr}]{\alpha} Th^{234} \xrightarrow[24.1\ \text{d}]{\beta} Pa^{234} \xrightarrow[1.18\text{m},\ 66.6\ \text{hr}]{\beta} U^{234} \xrightarrow[2.5 \times 10^5\text{yr.}]{\alpha}$$

The specific activity of U^{238} is 3.36×10^{-7} curies per g (i.e., 7.4×10^5 d/m/g), and at equilibrium the activity due to Th^{234} will be equal to the parent U^{238}. As 50% of the equilibrium concentration is reached after 1 daughter half life, a semi-continuous supply of the Th^{234} may be "milked" from a source of natural uranium, monthly "milkings" providing 4×10^5 d/m of Th^{234} for each gram of U^{238}.

For all practical purposes the long-lived U^{234} daughter terminates the decay sequence after Pa^{234}, thus avoiding further complications due to decay products. The high specific activity of Th^{234}, and consequent low chemical concentrations employed, usually make it desirable to add long-lived Th^{232} as carrier.

Method of Isolation of Th^{234}

Methods for the isolation of Th^{234} which have been described in the past include solvent extraction of the cupferrate complex at *p*H 8.0–8.5 into chloroform (*2*), multiple diethyl ether extraction of uranyl nitrate (*3*) in which case the uranium can be stored in a solution of ether (or other suitable solvent), and a combination of ion exchange and solvent extraction processes using nitrate solutions (*4*). The latter may take one of two forms: (1) Initial removal of the bulk of the uranium by ether extraction, followed by adsorption on a cation exchange column and removal of adsorbed uranium with hydrochloric acid. The thorium is then recovered with oxalic acid. (2) An initial concentration of thorium using a large cation exchange column, followed by further concentration and purification using a second cation column or by solvent extraction with tributyl phosphate (TBP).

Ion exchange techniques are desirable from an operational point of view, particularly by comparison with the diethyl ether methods which would involve the storage of large volumes of ether solution between "milkings," but initial concentration factors are lower. Comparison of the relative complex stabilities of uranium and thorium indicated by anion exchange studies in hydrochloric acid (*5*) and nitric acid (*6*) media clearly indicate the desirability of using the former, rather than nitric acid as advocated by Van R. Smit (*4*). An anion column would be expected to retain only the uranium from an uranium-thorium solution in HCl (>6 *M*), whereas a cation column would be expected to retain thorium almost exclusively.

Thus, for quantitative thorium isolation and concentration into a small volume a method similar to that of Van R. Smit (*4*) but using hydrochloric acid and smaller columns suggests itself. There still exists an objection to handling and storing relatively large volumes of acidic solution, but this may be overcome by holding the uranium on a large anion column and concentrating the thorium on a small cation column. This principle was applied as indicated below.

Small Column. A 50-ml buret with detachable plastic diaphragm stopcock and tip was used. A plug of glass wool was placed in the lower end of the buret and 50 ml of De Acidite FF,[2] −16 + 50 mesh was placed in the buret. A second glass-wool plug was placed on top of the resin bed. After the bed had been conditioned to the chloride form, two column volumes of 7 *M* HCl were passed through. Uranyl chloride in 7 *M* HCl (0.0986 gm U/ml) was passed through at a flow rate of 1 drop per 10 sec until breakthrough was observed (73 ml). Four column volumes of 8 *M* HCl were passed through and the combined effluent was analyzed for uranium. The capacity was thus determined as 6.5 g. During the conditioning and loading a 5% reduction in bed volume was observed. After a four-week period the Th^{234} was eluted with 50 ml of 8 *M* HCl

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[2] De Acidite FF manufactured by the Permutit Co. Ltd. is equivalent to Dowex 1 manufactured by the Dow Chemical Co.

containing 1 mg Th^{232} and concentrated on a small Zeo-Karb 225[3] column (capacity approx. 1 ml). The thorium was then eluted from the Zeo-Karb column with oxalic acid solution.

Medium Size Experimental "Cow." Following these preliminary experiments with the buret column, a Th^{234} "cow" having an anion bed volume of 600 ml was constructed from a 1-ft length of 2-in. diameter industrial "Pyrex" tubing. Black polythene $^1/_2$-in. i.d. pipe and fittings were used in the active circuit and upward elution adopted. The use of upward elution permitted the use of a completely closed circuit below the level of the top of the anion bed, minimizing the risk of a leak in the active circuit and the associated possibility of the bed running dry between "milkings." Operation was also simplified in that the active flow was controlled by the flow of inactive acid to the base of the column. Circulation of acid through the bed during milking was obtained by distillation. The advantages of this method are the absence of moving parts, simple flow control, continuous acid purification, and the fact that by simply limiting the total volume of acid in the circuit flooding is impossible as circulation ceases if the level in the evaporator drops below the heating element. For larger systems mechanical pumping would be more attractive.

The anion column was filled with − 16 + 50 mesh De Acidite FF and cycled from the Cl^- form to the OH^- form and back to the Cl^- form. Uranium (60 g) was then adsorbed on the resin bed from constant boiling HCl (approx. 70% of the full loading capacity).

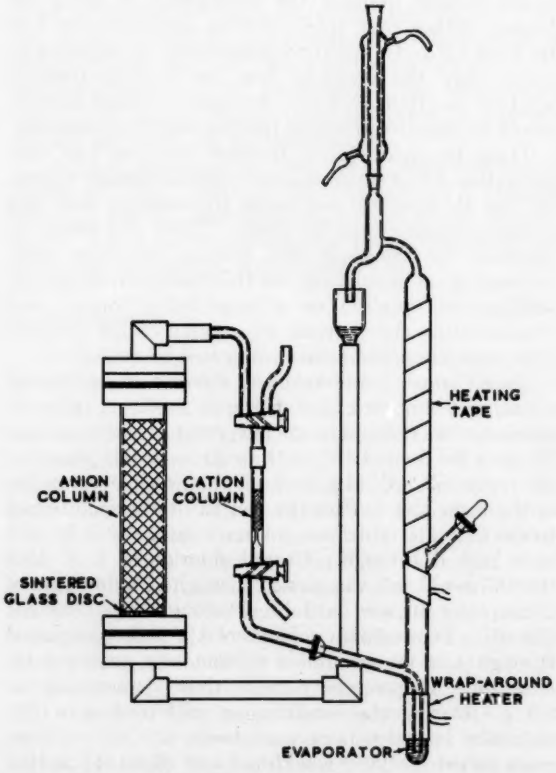

Figure 1. Apparatus for separation of Th^{234}.

[3] Zeo-Karb 225 manufactured by the Permutit Co. Ltd. is equivalent to Dowex 50 manufactured by the Dow Chemical Co.

A small Zeo-Karb 225 column (vol. 5 ml) in the overflow circuit (Fig. 1) served to concentrate the Th^{234} during operation of the "cow." The flow rate was adjusted to 3–4 ml per minute (i.e., less than one cation column vol. per minute) which also permitted $2^1/_2$–3 anion column volumes of acid to flow in one 8-hr working day.

"Milking" has now been carried out 3 times at monthly intervals. The procedure adopted was to add 1 mg of Th^{232} in HCl as carrier and switch on the evaporator and condenser water for one day, then to elute the thorium tracer from the cation column the following day with oxalic acid solution. The oxalate was then destroyed in solution with nitric acid and hydrogen peroxide to yield a Th^{234} solution in a nitric acid medium suitable for radiochemical tracer work.

Half life of Pa^{234}

Pa^{234} is a suitable isotope for the demonstration of half-life determinations. This isotope is a β-emitter with a half life of 1.18 min, and its decay product is the long-lived α-emitter U^{234} (half life 2.5×10^5 yr) so that no activity from subsequent daughter products will be present to complicate the experiment.

The short half life of Pa^{234} will furthermore: permit a complete half-life determination to be carried out in 10 min after the isotope has been isolated, and mean that equilibrium will be established with the Th^{234} parent in the same period, thus permitting successive experiments to be performed at 10 min intervals with Pa^{234} isolated from the same batch of Th^{234}.

Booth (*7*) has previously suggested this isotope for use in half-life determinations. His method of preparation was based on an ether extraction of uranyl nitrate solution with the formation of a Th^{234} radiocolloid and its adsorption and subsequent recovery from the walls of a glass vessel. The Pa^{234} was isolated from the parent Th^{234} by treating a Th^{234}-Pa^{234} source on a platinum tray with a few drops of concentrated HNO_3; evaporating to dryness followed by dipping the tray first into concentrated nitric acid for one second and then into distilled water. After blotting the tray with filter paper, the determination of the half life was attempted. Besides being chemically inelegant, quantitative yields in both Th^{234} and Pa^{234} stages are not possible and the method is not applicable to rapid successive protactinium isolations. A more elegant method has been developed from the previously described Th^{234} "Cow."

Operation without the cation column in the circuit concentrates the thorium in the evaporator as a chloride solution from which it can be removed and further concentrated into a small volume of HCl. In addition to the Th^{234}-Pa^{234} equilibrium mixture small amounts of desorbed uranium will also be present. Results reported by Peppard, Mason, and Gergel (*8*) show that under the acid conditions present, only uranium and protactinium will be extracted by TBP and this solvent was used to remove the small amounts of uranium present. In a matter of a few minutes the Th^{234}-Pa^{234} equilibrium is re-established.

In handling material of very short half life, speed in the isolation precedure and high yield are important, and for these reasons solvent extraction or special

ion-exchange (*9*) techniques are particularly advantageous. Of thorium and protactinium only the latter forms neutral or anionic chloride complexes and a number of solvents are suitable for the separation of these elements.

The Th^{234} "Cow" was run on one of its monthly milkings without a cation column. The Th^{234} solution in HCl which concentrated in the evaporator was removed and further evaporated under an infrared lamp to a volume of 3 ml. This was extracted with TBP to remove traces of uranium. Thereafter the Th^{234} stock solution was kept in a 10-ml centrifuge tube and the Pa^{234} extracted as required.

While TBP can be used as the extractant, better results were had with 40% tri-*n*-octylamine in xylene and with diisopropyl ether as solvents. The latter is particularly attractive as phase separation is very rapid, and this obviates the need to employ a centrifuge and also reduces the time necessary for the separation. In all cases the organic and aqueous phases (3 ml of each) were stirred vigorously with a laboratory stirrer for 2 min; the phases were separated using a centrifuge where necessary. The organic phase was then removed with a pipet placed in a second tube and given a brief (approximately 15 sec) wash with an equal volume of 6 *M* HCl. After phase separation, the organic phase was transferred to a polythene cup and counted in a well type scintillation counter connected to a rate meter. The total time required for the chemical separation was between 1–2 min after the initial stirring with the thorium solution was discontinued. The procedure could be repeated at approximately ten-minute intervals by which time equilibrium between Th^{234} and Pa^{234} had been re-established.

Experimental results obtained for several runs are shown in Figure 2. In one case the Pa^{234} was backwashed from diisopropyl ether with 6 *M* HCl containing a trace of HF. The low count rates observed in this case are chiefly due to the additional time required in the chemical separation.

The logarithmic plot of count rate against time in Figure 2 indicates a half life of 1.3 min which is in reasonable agreement with the generally accepted value of 1.2 min. The slight increase in the value of the half life is attributed to the response time of the integrating circuit of the rate meter.

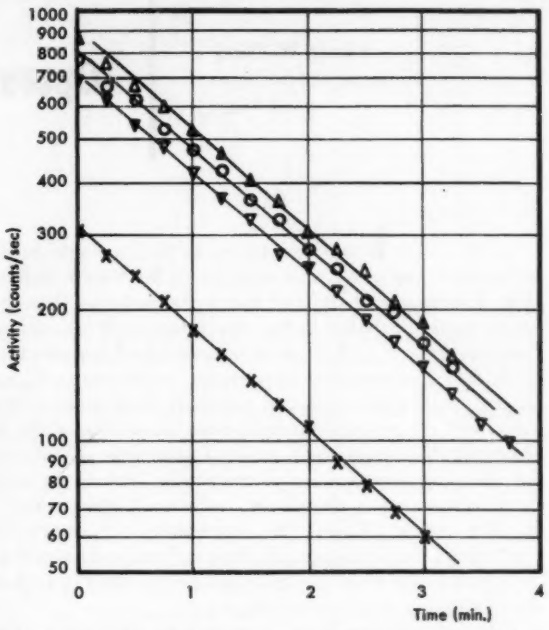

Figure 2. Decay of Pa^{234}. Δ and ∇ = 40% Tri-*n*-octylamine/xylene solvent. ○ = Diisopropyl ether solvent. × = Diisopropyl ether solvent and backwashed into HCl—HF.

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Division of CHEMICAL EDUCATION

American Chemical Society

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Operational Inorganic Chemistry

If one were to try to pick a single event in recent times which was responsible for the revitalization of inorganic chemistry, the writer believes that the event would probably be the development of fission and fusion reactions. Here are processes which are spectacular and of tremendous importance to humanity (good or bad) and which demand for their development the very best of our experimental and theoretical skills in the separation and classification of materials. Methods for effecting a separation of materials (and as a consequence rare earth chemistry) advanced spectacularly in this work. Even the cornerstone of inorganic chemistry, the periodic table, was revised and extended. It is significant that this renaissance was closely tied to developments in modern physics.

The pattern has been repeated many times. The development of electron paramagnetic resonance by the physicist led to the revival of earlier models for the interpretation of detailed magnetic data on coordination compounds. The now classical works of Bethe and of Van Vleck were rediscovered, and modern ligand field theory terminology became a must for the inorganic chemist. The Nobel-prize-winning development of nuclear magnetic resonance by Purcell and Block has been extensively applied in inorganic chemistry. Finally regular developments in the perennial problems of theoretical physics and chemistry provide an ever expanding theoretical framework into which the facts of inorganic chemistry must be placed, and the terminology, which changes with the fashions of the day, must be kept modern.

Caught in this close relationship with present day physics, inorganic chemistry is assuming a more distinctly physical tone, and it is not unexpected nor improper to note that most lecture courses in advanced inorganic chemistry are going farther and farther into the realm of modern physics. The situation will be healthy as long as a firm relationship is maintained between the theoretical concepts of physics and the facts and concepts which *are* modern inorganic chemistry. The situation becomes undesirable when the inorganic chemistry course becomes a nonmathematical presentation of modern physics and when terminology borrowed from the theorist is glibly used as a physical explanation for processes which are too complex for rational treatment by available theoretical methods. Recent texts and reviews might be cited in which real inorganic chemistry can be recognized only with difficulty in the bewildering array of bond orbitals and hypotheses. It is not uncommon for new terminology to be introduced so rapidly that the student (and perhaps even the instructor) fails to appreciate its true physical meaning and operational background. Frequently, predictions based on classical periodic analogies or contrasts are buried in the modern fashionable terminology to such an extent that the real underlying periodic relationships may be lost, and postulates of doubtful validity are substituted. It is important to remember that our most effective predictions in inorganic chemistry are usually based on analogy.

Lest the above remarks be interpreted as a self-righteous blast at my colleagues, let me hasten to add that I recognize in the above charges large sections of my own graduate and undergraduate lecture program. This fact among others has been the basis for, in the words of our leaders, "an agonizing reappraisal" of present methods and trends. It is not the purpose of this paper to suggest a complete revision of our lecture methods, particularly since I could not subscribe to a program which abandons our present semitheoretical approach and our happy marriage with modern day physics. Operational *expansion* of theoretical concepts would seem to be far more effective than drastic surgery and reversion to simple empiricism.

The laboratory, which unfortunately seems to be the vanishing prairie of inorganic instruction, seems well suited for the task of bringing the lecture material into the traditional realm of the inorganic chemist: the preparation of materials and the classification and correlation of their properties in terms of fundamental concepts. Many worthwhile laboratory courses have been described and many more will be. The following is a description of only one approach to the problem; it is described here with no claims for superiority or infallibility, but as an earnest attempt to bridge the gap between inorganic chemistry as many of us teach it in the lecture room and inorganic chemistry as we find it in the research laboratory. Two units will be considered. The first is an optional 2-semester-hour undergraduate laboratory course which is offered in conjunction with a 2-hour lecture course in inorganic chemistry for seniors. The second is an optional 2-semester-hour laboratory course in advanced inorganic chemistry which is offered in conjunction with a special topics course in inorganic for graduate students.

The Undergraduate Course

The undergraduate lecture course is more or less conventional in character. Theoretical models of the atom and of compounds are developed extensively. This work is followed by a rather extended discussion of

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the periodic table which includes consideration of systematic trends in stability of oxidation states in Bohr's four groups of the table. Inorganic stereochemistry, silicate chemistry, acid-base systems, alkali metals and thermochemical cycles, oxidation and reduction, and a brief introduction to coordination chemistry are usually included.

The laboratory work which parallels the lecture course makes an attempt to lay a broad foundation for synthetic work in inorganic chemistry while illustrating the lecture material. The course stresses the general methods and techniques of synthesis and is more or less traditional in character. For example, crystallization is considered in terms of the phase rule and phase diagram. The approach is an extension of that suggested by Walton (*1*). Double salt formation and some purification processes are used as examples. The properties of alums may be related to sizes of ions (*2*), and our success or failure in purification of a double salt by recrystallization may be related to the phase diagram (*1*). Similarly the failure of recrystallization as a purification procedure in many cases may be related to isomorphous substitution of similar ions in the lattice. The example of $FeSO_4$ in $CuSO_4$, given by Henderson and Fernelius (*3*), is a pertinent one, and the rare earths provide a classic illustration of this problem.

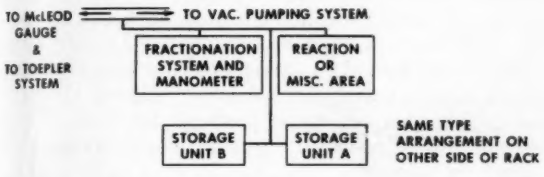
TO McLEOD GAUGE & TO TOEPLER SYSTEM
TO VAC. PUMPING SYSTEM
FRACTIONATION SYSTEM AND MANOMETER
REACTION OR MISC. AREA
STORAGE UNIT B
STORAGE UNIT A
SAME TYPE ARRANGEMENT ON OTHER SIDE OF RACK

Figure 1. Block diagram of student high vacuum system.

Alumino-thermic type reductions are carried out, and materials such as crude "boron" and "silicon" (actually these products are far from being pure elements) prepared in the operation are frequently used in subsequent hot tube reactions for the preparation of $SiCl_4$ and BCl_3. Good operational techniques and simple glass blowing procedures are required in order to get the halides into sealed tubes. Pure BCl_3 may be stored in the freezing compartment of the refrigerator in glass tubes. Its storage in sealed glass tubes at room temperature is *not* recommended, particularly when amateur glass blowers have been involved.

The preparation of these and other halides can be used to illustrate the systematic variation in the stability of oxidation states in the different parts of the periodic table. For example, the reaction of chromium metal with chlorine to give $CrCl_3$ and the reaction of

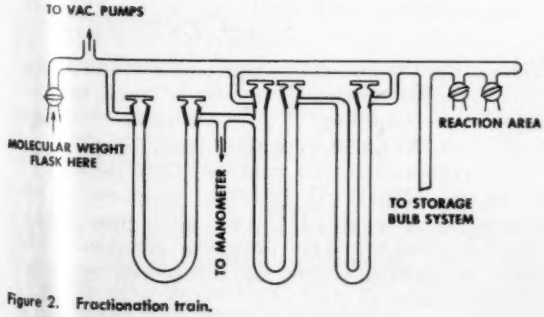

Figure 2. Fractionation train.

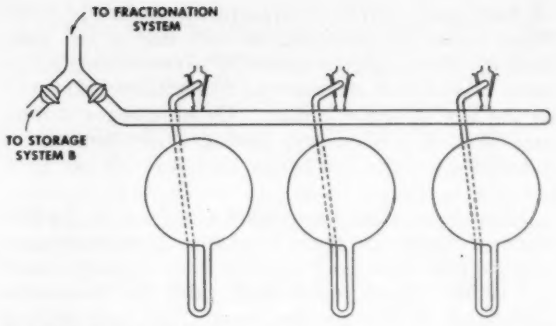

Figure 3. Storage unit.

tungsten to give WCl_6 under comparable conditions emphasize the fact that higher valence states become more stable as one goes down in a transition group (Bohr's group III). The formation of relatively stable $SiCl_4$ and unstable $PbCl_4$ brings out the fact that the stability of the maximum oxidation state falls as one goes down a group of the typical elements (Bohr's group II). Electrolytic reduction of $TiCl_4$ and oxidation of $CoSO_4$ help to emphasize the fact that the lower oxidation states are becoming more stable as one goes across from left to right in the transition elements. All of the foregoing laboratory observations can be correlated with the discussion of atomic structure and the discussion of ionization potentials. It is mandatory, however, to point out to the student in subsequent work, such as that on thermochemical cycles, that the problem is a complex one and we really employ a fortunate correlation rather than an absolute explanation of the descriptive chemistry. The synthesis of coordination compounds can be tied to the coordination compound discussion, acid-base theory, and oxidation-reduction procedures.

A conscientious attempt is always made to correlate lecture discussion and its chemical consequence as it appears in laboratory operation. Since it is not possible for one student to do all of the experiments needed for the correlations, each student is assigned a set of experiments and group data are used to make correlations in weekly discussions.

The Graduate Course

The graduate laboratory course is closely tied to a special topics course which includes a discussion of: the hydrides, some aspects of rare earth chemistry, and coordination compounds. The optional 2-hour laboratory course associated with the special topics lecture work is less conventional in nature and includes: vacuum technique which is essential to hydride manipulation, magnetic measurements, and systematic transformation of coordination compounds.

Approximately 50–70% of the course time is usually spent on vacuum techniques, since this is frequently a new area to our students. Sanderson's book (*4*) on vacuum manipulation is strongly recommended as a working manual; only the student can provide the requisite practice.

The vacuum line is represented diagrammatically in Figures 1–3. It includes: mechanical and mercury diffusion pumps, a McLeod gauge, a 3-trap distillation train, and a Toepler pump which can be removed from the system. The mechanical and diffusion pumps, the

McLeod gauge, and the Toepler pump service two distillation trains, one mounted on each side of the rack. Each distillation train is connected to two sets of storage bulbs. With this arrangement two students can work on the line at any one time. By assigning a storage unit to each student and having students work on different days, one can handle four students per week per rack.

All students, after their earlier experience in the first semester course, are urged to practice glass blowing in order to gain proficiency in the making of simpler seals and bends. These rudimentary skills find immediate application in vacuum line work. The instructional program includes: calibrating the volume of the traps, measuring a temperature-vapor pressure curve on a pure *known* compound and a molecular weight by vapor density, separating the components of a known mixture and measuring molecular weight and vapor pressure on each component for identification, separating, and identifying the components of an unknown mixture, and running a simple reaction which demands, at some point, an application of the foregoing techniques.

Ammonia is frequently used as a known for the initial measurements, and unknown mixtures such as NH_3—$(C_2H_5)_2O$, PH_3—$(CH_3)_2O$, $ClCF_3$—$ClCHF_2$, SF_6—$C_2Cl_2F_4$, etc., have been successfully separated and identified by students. The vapor pressure tables by Stull (*5*) are the standard reference. The following reactions have been used successfully to illustrate vacuum technique:

$$Hg(CN)_2 \xrightarrow[N_2]{\Delta} Hg + (CN)_2$$

$$4PCl_3 + 3LiAlH_4 \rightarrow 4PH_3 + \overbrace{3LiCl + 3AlCl_3}^{?}$$

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + \text{Residues}$$

$$P_2I_4 + NaBH_4 \rightarrow PH_3 + \text{Residues}$$

$$PH_3 + Na \xrightarrow[NH_3]{\text{lig.}} NaPH_2 + {}^1/_2H_2$$

The work on the reaction may be a small research project wherein detailed answers are not available but where pretty well defined results are expected (for example, the fourth reaction above), or it may be a well known process (for example, the second reaction).

The magnetic susceptibilities of compounds and the magnetic moments of the constituent atoms can usually be discussed glibly by many students of chemistry, and most students at the senior level are well acquainted with the frequent assumption that the magnetic moment can serve as a convenient measure of the number of unpaired electrons in a material. It is somewhat disturbing then to find that these same students have no appreciation for the experimental and physical implications of magnetic terminology and are completely unaware of the simplifications and assumptions (both theoretical and practical) which are involved in the treatment of experimental magnetic data for the usual transition elements. The transition between theoretical models and physical reality is rarely made without strong urging by those of us charged with student teaching. The simple and inexpensive method described by Schuler (*6*) permits the easy measurement of magnetic susceptibilities, and the calculation of moments from the data can provide a better appreciation of the variables in the collection, and treatment, of data. Furthermore, a measurement on a rare-earth salt can do much to dispel erroneous ideas concerning the validity of "spin only" relationships for general magnetic moments, and the results provide an excellent point of departure for the development of ligand field theory in lecture. Weak field, strong field, and very strong field cases are more easily visualized in terms of experimental examples from laboratory operation.

Finally, most students in an inorganic chemistry course take readily to the drawing of an octohedron and to the writing of d^2sp^3 hybridization symbols. On the other hand, methods of synthesis of common coordination compounds and systematic methods by which changes in the structure of penetration type coordination compounds can be achieved are less well understood. Though much of our information in this area is still rather sketchy and nonsystematic in character, certain type reactions and contrasts can be proposed for a few specific systems. Such classification, though not all inclusive, will at least provide a pattern for an analysis of many of our synthetic procedures and will provide an experimental background for many of the terms used in coordination chemistry.

As a case in point, it is of interest to compare procedures for preparing $[Cu(NH_3)_4]^{++}$ and $[Co(NH_3)_6]^{+++}$. Since $[Cu(NH_3)_4]^{++}$ forms and dissociates reversibly as NH_3 is added to or removed from a solution of a Cu(II) salt, it is a most convenient illustration of the so-called "normal," or "labile," type of coordination compound. In contrast, procedures for preparing $[Co(NH_3)_6]^{+++}$ and $[Cr(NH_3)_6]^{+++}$ illustrate clearly the slower, non-reversible methods involved in the preparation of so-called "penetration," "robust," or "inert" complexes.

The chemistry of cobalt and chromium ammines is of particular interest in a discussion of synthetic methods. Since cobalt is most commonly divalent in its noncomplexed state, the Co(II) salts provide a logical starting point for the synthesis of Co(III) coordination compounds. Oxidation by air or H_2O_2 is effected in the presence of the amine and its salt. For ammonia the equation is

$$2Co^{++} + 2NH_4^+ + 10NH_3 + {}^1/_2O_2 \xrightarrow{\text{Charcoal}} 2[Co(NH_3)_6]^{+++} + H_2O$$

In contrast to the previously mentioned case of $[Cu(NH_3)_4]^{++}$, the formation of the $[Co(NH_3)_6]^{+++}$ is neither rapid nor reversible. In the absence of the charcoal, water or the anion in the solution frequently enters the coordination sphere; thus the following equation is typical if charcoal is omitted in a solution containing chloride:

$$2CoCl_2 + 2NH_4Cl + 8NH_3 + {}^1/_2O_2 \rightarrow 2[Co(NH_3)_5Cl]Cl_2 + H_2O$$

The charcoal promotes the conversion of the pentammine to the hexammine. If ammonium carbonate is used in place of NH_4Cl and $Co(NO_3)_2$ is used as the original Co(II) salt, the product is largely $[Co(NH_3)_4CO_3]^+$. If NH_4Br is present in a cold solution, $[Co(NH_3)_5H_2O]^{+++}$ is formed. Finally if NH_4NO_2 (prepared *in situ*) is used in place of NH_4Cl, the same process yields $[Co(NH_3)_3(NO_2)_3]$. The foregoing compounds may serve as starting points for subsequent systematic transformations (*7*).

The chemistry of chromium would appear to bear little direct relationship to that of cobalt since chromium is normally trivalent or hexavalent in commercially available starting materials. Indeed most procedures for the synthesis of $[Cr(en)_3]^{+++}$ or $[Cr(NH_3)_6]^{+++}$ involve reaction of the anhydrous chromium (III) salt with the anhydrous amine, a process which is unsuitable for cobalt complexes since simple Co(III) salts are not readily available.

$$CrCl_3 \text{ (anhyd.)} + 6NH_3 \xrightarrow[NH_3 \text{ liquid}]{KNH_2^+} [Cr(NH_3)_6]Cl_3$$

$$Cr_2(SO_4)_3 + 6 \text{ en} \xrightarrow[\text{ethylene diamine}]{\text{heat}} [Cr(en)_3]_2(SO_4)_3$$

On the other hand, Balthis and Bailar (*8*) noted that aqueous solutions of chromium(II) salts are oxidized in the presence of an amine to give the corresponding chromium(III) complex. The reaction bears a strong formal similarity to the standard reaction used to prepare Co(III) complexes. The hydrogen ion serves as the oxidizing agent rather than air or H_2O_2. Both ammonia and ethylenediamine can serve as the amine.

$$2Cr^{++} + 2NH_4^+ + 10\ NH_3 \rightarrow 2(Cr(NH_3)_6]^{+++} + H_2$$

Berman (*9*) found that in the absence of a catalyst the above procedure, in his hands, usually gave a red oil and very low yields of the yellow $[Cr(NH_3)_6]^{+++}$, but yields of complex were quantitative if platinized platinum was added to promote H_2 liberation. Such observations illustrate both the advantages and weaknesses of a systematic arrangement of preparative procedures. A systematic framework aids in the development of the similarities of reaction chemistry and provides a simple working generality, but one cannot rely too heavily upon the "system" or generality and neglect the essential differences in the chemistry of the individual elements. Indeed I am of the opinion that emphasis upon the foregoing similarities and experimental differences would do much to add meaning to our usual theoretical discussions of "bond type" and to our proposed classification of reactions on the basis of reaction mechanism. The importance of such basic experimental observations in compound classification was clearly recognized by Taube (*10*) in his excellent review on the mechanism of substitution reactions.

The systematic transformation of the above coordination compounds can be examined under two headings: the changing of groups *outside* the coordination sphere and the changing of groups inside the coordination sphere. Both processes emphasize the high energy barrier in the usual formation and decomposition processes for the penetration complexes.

For changing groups outside the coordination sphere, standard systematic procedures for salt conversion are usually applicable. Thus a halide can be converted to a hydroxide through the standard technique of grinding with silver oxide. Typical equations are:

$$2[Co(NH_3)_6]Cl_3 + 3Ag_2O + 3HOH \xrightarrow[\text{cold}]{\text{ice}} 6AgCl + 2[Co(NH_3)_6](OH)_3$$

$$2[Co(en)_3]Cl_3 + 3Ag_2O + 3HOH \rightarrow 6AgCl + 2[Co(en)_3](OH)_3$$

Neutralization of the resulting hydroxide with an acid produces a new coordination compound. The titration curves for the neutralization processes are easily made and demonstrate the fact that $[Co(NH_3)_6](OH)_3$ and $[Co(en)_3](OH)_3$ are strong bases with 3 strongly ionized OH^- ions per molecule

$$[Co(en)_3](OH)_3 + 3HX \xrightarrow[\text{soln}]{\text{cold}} [Co(NH_3)_6]X_3 + 3H_2O$$

Alternatively, direct metathesis reactions may be employed in selected cases to transform groups outside the coordination sphere:

$$[Cr(NH_3)_6]Cl_3 + 3AgF \rightarrow [Cr(NH_3)_6]F_3 + 3AgCl$$

The inert nature of the complex group is clearly apparent. Such synthetic methods have been useful in this laboratory in preparing fluoride salts of coordination compounds for research purposes (*11*).

Systematic procedures for transforming groups inside the coordination sphere may likewise be based upon an application of conventional inorganic reactions to appropriate starting complexes; reactive groups placed strategically inside the coordination sphere serve as a point of attack. For example, the carbonate ion in $[Co(NH_3)_4CO_3]^+$ and the three nitrite groups in $[Co(NH_3)_3(NO_2)_3]$ may be replaced by the action of an appropriate acid. The chloride ion in $[Co(NH_3)_5Cl]^{++}$ can be removed slowly by the action of Ag^+ in hot solution, but the procedure has limitations; a more effective but less obvious procedure for removing chloride involves dissolving the chloropentammine in warm aqueous ammonia; the aquopentammine is produced and may be crystallized from a cold acid solution. The water in $[Co(NH_3)_5H_2O]^{+++}$ is then rather easily replaced by a variety of coordinating agents.

The above attempts at systematization obviously neglect many critical details and, indeed, the procedures suggested may not always be applicable for the synthesis of a given desired product. On the other hand, such an arrangement of information provides a reasonable point of departure for the detailed study of a specific system, and the laboratory experience is of high educational value.

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Forty Hours to the Inorganic Frontier

A literature assignment in inorganic chemistry

A senior student may have an intriguing view of inorganic chemistry. He has had general chemistry, and in this course he was exposed to physical concepts and the application of mathematics to a variety of problems. This course was diluted with a minimum of descriptive inorganic chemistry. The student enjoyed qualitative analysis because it presented something of a challenge and he learned a few chemical reactions and the chemist's deductive method of reasoning.

The challenge of analytical chemistry was worn a little thin in quantitative analysis by the time-consuming operations. In organic chemistry, he was amazed to find that the field developed so logically, and he recognized the possibilities of preparing new, interesting compounds. Physics, mathematics, and physical chemistry seemed to fall into proper perspective.

He has had two years of German, and for the use he has made of it he is wondering why? If he has had a course in library science, he knows where the books are but not the limitations and contents.

To this student, inorganic chemistry does not amount to much. Based on his course in general chemistry, it seems to be the ultimate in disorganization. He has heard the names of 102 elements but remembers only 52. If he is to graduate with a clear concept of inorganic chemistry, he should have an inspirational type course in his last year of college.

The following could well be the objectives of such an advanced inorganic course: (1) make the field sufficiently logical to be palatable; (2) clarify inorganic nomenclature; (3) use concepts of structure to develop the periodic table and thereby give the student a mechanism of comparison to help remember and to predict the nature of chemicals and reactions; (4) apply physical concepts of structure, bonding, ionic radius, etc., to help explain the why of reactions and structure; (5) expand the field for the student by opening the areas of complex compounds, solvent systems, and other special topics; (6) provide historical background to make the course cultural as well as factual.

The first five are well covered in the few advanced texts, but the end products of chemistry, its compounds, are neglected. Methods and mechanisms are necessary and interesting, but the great percentage of chemists in the United States live off the products. Descriptive chemistry should not be overlooked.

A teaching method we have found successful is to assign a specific anion to each student taking the advanced inorganic course. We provide him with a blank periodic table on which he will record all of the compounds of that ion that have been reported in the literature. He will submit a term paper giving a summary of the properties of the central element, then the acid, then each compound. For each cation he will use a separate sheet and record the data in an organized fashion so that the comparisons can be made from page to page. All references are to be shown, as well as methods of preparation, yields, and physical data. After this study is complete, the student must provide a summary section in which he predicts what compounds could be made, how to make them, and the properties of these compounds. The student should note the gaps in the literature for physical data, such as X-ray, thermodynamic, etc.

Starting with Lange's "Handbook of Chemistry," the student then goes to Remy, then to Mellor (and its reference problem), then to Jacobson's "Encyclopedia of Chemical Reactions," and finally to Gmelin and an experience with German. Dates of publications of the Gmelin volumes must be noted as an indication of when to start using the abstracting journals. Since the listing of the compounds is generally under the cation heading, the student must become familiar with most of the volumes of Gmelin. It is assumed that all library aids will be used including interlibrary loan. Industrial concerns active in the field can be called upon for data.

By now the student is at the "Frontier." He knows much is yet to be done and has a new insight into the field. Interest grows as he presents his findings in a one-hour report to the other students.

Students do a presentable job in 40 to 50 hours. The instructor must spend at least four hours checking each anion before assigning it in order to avoid blind alleys. Time must be spent in the library with the student, preferably after he has struggled for a few hours. Respect must be shown for the older literature; it is often the only reference.

The less familiar ions are the best to assign because the student finds more gaps in the literature. Typical of good assignments are selenite, selenate, telluride, tellurite, ferrite, hexachlorosmiate(IV), and perrhenate.

If one wishes to develop interest in inorganic chemistry, this "Anionic Approach" will bring his students in forty hours to the "Inorganic Frontier."

Presented as part of a symposium on Instruction in Inorganic Chemistry, sponsored jointly by the Divisions of Chemical Education and Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958. For other papers in this series see THIS JOURNAL, 36, 441 (1959).

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Models for Demonstrating Electronegativity and "Partial Charge"

The instructional usefulness of extending the concept of electronegativity to the estimation of partial charges on combined atoms has been discussed in a series of earlier papers in THIS JOURNAL (*1*, *2*, *3*, *4*). There have also appeared descriptions of a periodic chart showing atomic electronegativities by color (*5*) and of two-dimensional representations of molecules showing partial charge by color (*6*). One purpose of this paper is to report the extension of these applications of color to models which now permit in three dimensions a new visualization. A second purpose is to re-emphasize, on the basis of continuing experience, the unique teaching value of such models and of the fundamental principles which they dramatize.

Teaching the Periodic Law

The Periodic Law and the valence relationships of the elements can be illustrated using new atomic models made of foamed polystyrene spheres. A convenient scale is 1.5 in. per Ångstrom, which, if covalent radii are used, makes an atom of hydrogen (smallest) about an inch in diameter and an atom of cesium (largest) about seven inches in diameter. The spheres may be painted with tempera, if a wetting agent such as a modern dishwashing detergent is added to the water medium, and when dry may be sprayed with a light coat of clear plastic finish. For reasons to be explained below, the color scale recommended for electronegativities is not that suggested for the original chart (*5*). Instead, red represents lowest electronegativity, yellow intermediate, and blue highest. The complete scale may use as many as 25 hues from red through oranges and yellow and greens to blue. Grey is used for the inert elements. A piece of stiff wire thrust entirely through the center of an atomic sphere can be formed into a loop at one end and a hook at the other. The plastic may be protected from wear at the points of wire entry by small washers imbedded in and glued to the plastic. Half-inch diameter spheres may be glued to the atomic sphere to represent outermost electrons (white) and electron vacancies (black). These may be placed in pairs at locations showing valence structure, this being more usefully informative than ground-state structure. For example, three pairs of small spheres (one white and one black in each pair) are fastened at the corners of an equilateral triangle in plane with the nucleus to represent the directional characteristics of sp^2 hybrid bonds on the models of B, Al, Ga, In, and Tl. (For the transition elements, electronegativity is known only very approximately, and the valence structure is too variable for simple representation by "electrons" glued to the models.)

Models of atoms of the first 20 elements are adequate to introduce the subject of periodicity. One method of presentation is to take these models out of a box and distribute them at random on the lecture bench. Then, following the founders of the Periodic Table, one can arrange these in order of increasing atomic weight. Hooked together, they form a colorful chain nearly seven feet long. The fact of periodicity becomes thus spectacularly obvious. Not only is the periodic variation in size immediately evident, but students can see too the periodicity of valence electrons. Most striking

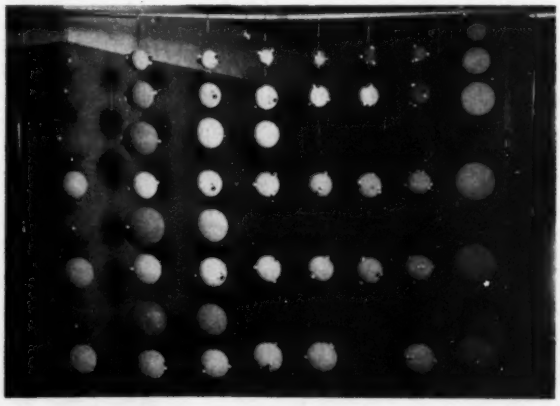

Figure 1. Periodic arrangement of atomic models.

of all is the display of electronegativity variations, the change, for example, from red Li through orange Be, yellow-orange B, and yellow-green C to green N, greenish-blue O, and blue F, and then to grey Ne being nearly repeated by the sequence from red Na through orange-red Mg, orange Al, and yellow-orange Si to greenish-yellow P, yellowish-green S, and blue-green Cl, and then to grey Ar.

Having pointed out all apparent aspects of periodicity, one can then proceed to disconnect the spheres and reconnect them in similar, vertical groups as in a periodic table. A frame from which these groups can be suspended is easily made from a pair of music stands and a six foot crossbar of one-inch aluminum tubing or, even less expensively, from lumber. The "diagonal relationships" will be especially conspicuous, Al being nearly the same color as Be, and Si as B. Additional elements may then be attached to make a

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more complete "table." Such a table, an example of which appears in Figure 1, can be permanently displayed in the lecture room, where frequent reference to it can be very helpful in explaining chemistry. Individual atomic models can quickly and easily be disconnected for special discussion, as in considering the specific chemistry of the individual elements.

Molecular, Ionic, and Crystal Models

The representation of partial charge by color gives a unique utility to molecular models (*6*). Instantly one can tell not only the structure but also the polarity of each bond, visualizing not merely the direction of polarity but also its relative extent. Such information can of course be extremely helpful toward understanding the physical and chemical properties of the compound. Three-dimensional models can be constructed from foamed polystyrene spheres fastened together, after painting, by combination of glue and wooden connectors. The only structural features of a molecule or crystal known with reasonable certainty are the bond lengths and bond angles. The extent to which the individual atoms are considered to contribute to the space effectively occupied by the molecule or crystal depends on a certain arbitrariness of definition and measurement. The choice of atom sizes, or even of a spherical shape for the atoms, for the models is therefore somewhat arbitrary, requiring rigorously only that the bond angles be correct and the distances between sphere *centers* be accurately to scale. The models most commonly employed in teaching and used mainly in organic chemistry are designed to represent the van der Waals radii of the atoms which show the "closest distance of nonbonded approach." This is desirable where steric relationships are to be emphasized and where partial charges and bond polarities are generally relatively low. The models recommended for use in inorganic and general chemistry, however, have atoms with sizes representing the smaller, covalent radius, or distance of single bond approach. Not only are covalent radii more reliably known, but the following advantages favor their use: (a) they permit ready differentiation of single and multiple bonds, represented by tangential or closer than tangential approach of the two spheres; (b) the models are more open in structure and permit viewing the interior of more complex aggregates whereas if the outside atoms were of van der Waals radii they might block out the interior entirely; (c) the covalent radius indicates the distance of approach necessary for bond formation and therefore chemical reaction and is thus at least as significant for its purpose as the van der Waals radius; (d) differences in size associated with partial charge are easily estimated (*7*) and shown when covalent radii are used. And, incidentally, models using covalent radii are generally much simpler to construct.

The color scale chosen to represent partial charge may be consistent with that used to represent electronegativities if yellow stands for zero charge, red for high positive, and blue for high negative charge. The consistency is limited because the electronegativity of course is not identical with its result, the partial charge. However, with this charge-color scale, an atom of low electronegativity (red) is most likely by chemical combination to become positive (red), and an atom of high electronegativity (blue) is most likely to become negative (blue).

For models easily visible throughout a large lecture room, the same scale suggested for the atomic models, 1.5 in. per Ångstrom, is recommended.

The "Partial Charge" Concept

Before detailing some representative applications of the new models, it should be helpful to review the basic concepts upon which partial charges are estimated and to consider exactly what these "charges" represent.

In brief, atoms of different elements differ both in the strength with which they resist removal of their own electrons and in their attraction for outside electrons. These properties are displayed jointly as the fundamental quality called electronegativity, which is most commonly the major factor determining the relative degree of sharing of electrons by two atoms covalently joined together. If the bonded atoms are unequal in electronegativity, the valence electrons will spend more than half the time more closely associated with the initially more electronegative atom, thereby giving it a partial negative charge and leaving the other atom partially positive. Charges thus resulting from uneven sharing of valence electrons can be estimated by a simple and reasonable method (*4*) based in part on the recognition that electronegativity must change with acquisition of charge, decreasing with negative and increasing with positive, and on the assumption that such change is linear with amount of charge.

Now, knowing molecules to be composed of two or more "point" positive charges in relatively fixed positions, imbedded in a diffuse cloud of electrons, one can recognize that the assignment of partial charges to the individual atoms must at best be only a deliberate simplification. It is indeed an attempt to describe an exceedingly complex system in terms useful toward reaching a practical understanding of the molecule. Ultimately, the validity of such an attempt must be judged by its success in explaining and predicting chemical properties and phenomena. Charge data for more than two thousand compounds and ions, including most of the more familiar substances of inorganic chemistry, have now been calculated and studied. These data make possible a more coherent, logical, consistent organization of inorganic chemistry than has heretofore been available.

The widespread acceptance of quantum mechanics as a pathway to ultimate fundamental truth in chemistry has to some extent inhibited recognition of the possible utility of a simpler, less rigorous, but more practical approach. However, the new charge data are not in serious conflict with other theoretical concepts of chemistry; for example, wave mechanical descriptions of bonding recognize and attempt to take into account "ionicity." Indeed, the charge data serve, for the most part, simply as a quantitative expression of what experienced chemists have qualitatively and intuitively long believed to be true.

Furthermore, these data are reasonably consistent with various physical measurements believed to indicate similar electrical dissymmetries. Dipole moments are so sensitive to other factors besides initial electronegativity differences that only in the simpler (mainly diatomic) molecules can even rough consistency with

calculated partial charges be expected, but for such molecules the agreement is remarkably good. Other physical evidences consistent with partial charge data have recently been obtained from microwave spectroscopy and from studies of nuclear magnetic resonance.

All these physical data, when considered together with the properties of compounds, strongly support the conclusion that the condition of a combined atom does indeed depend on its environment, which to a large and usually dominant extent results from electronegativities. One may call this contribution "partial charge" or by any other name, as long as its true significance is clearly understood: *"Partial charge" is a quantitative estimate of the relative extent to which differences in electronegativity of the atoms before compound formation have altered the electronic field about the nucleus of an atom in a compound.* In the following discussion it will become apparent that as *an index of the condition of a combined atom*, partial charge provides a uniquely useful and satisfactorily reliable basis for explaining much of chemistry.

An advantage in the new models of representing charge by color is that it transfers emphasis from the *numerical* charge quantities to the *relative condition* of combined atoms, which is of more fundamental significance.

Physical Nature of the Elements

The physical properties of the elements, as well as the chemical properties, are of course a reflection of the atomic structure, but only indirectly. Directly, these properties are a consequence of the physical nature of the elements, determined by the way the atoms are *combined*. For example, sulfur is a low-melting, volatile solid not by direct reason of its particular atomic structure but because it is composed of S_8 molecules, the intermolecular attractions of which are relatively weak and easily overcome by heat. Nitrogen is chemically unreactive not by virtue of an inert atomic structure, which it does not have, but because the interaction of

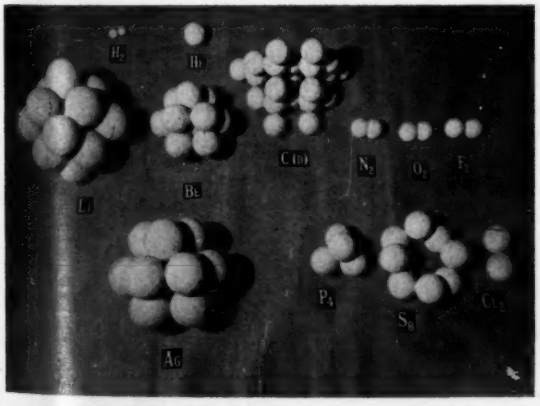

Figure 2. Models of some elements.

two nitrogen atoms forms so stable a molecule that the disruption usually needed for its chemical reactivity is extremely difficult. Such properties can be understood much more readily with the help of models of the elements, such as shown in Figure 2. The physical transition from metal through high-melting nonmetal to very low-melting gas, for example, is shown very well by the models from lithium through fluorine. All these models are of course colored yellow, indicating nonpolar bonds.

Chemistry via the Nonmetals

The entire periodic system can conveniently, and in many respects most instructively, be surveyed from the viewpoint of the nonmetals. A systematic application of the concept of partial charge to the chemistry of nonmetals shows that both physical and chemical properties of their compounds can be quite consistently understood in terms of the condition of the combined nonmetal atoms. Two useful principles apply: (1) many reactions can be explained as evidences of a tendency for an atom of an active nonmetal to abandon its combination with one atom to join another from which it can acquire higher negative charge; (2) other factors

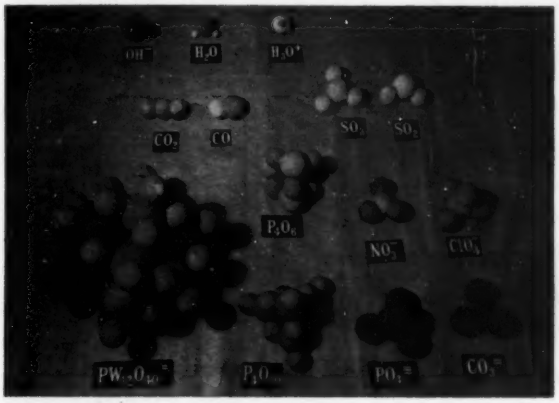

Figure 3. Some oxides and oxy-ions.

being equal or negligible, an atom can act more readily as an electron donor the higher its negative charge. Illustrations of these principles will be found in the following brief discussion of binary and complex compounds of oxygen, hydrogen, and chlorine.

Oxides (*Fig. 3*). The most important oxide is water and models of water molecule, hydroxide ion, and hydronium ion have a multitude of uses in teaching chemistry. Such models show the oxygen to be smallest in H_3O^+ ion, larger in H_2O, and largest in OH^- ion. In H_3O^+, the yellow-green color of the oxygen shows it to be only slightly negative and therefore of considerable residual oxidizing power but little capability as an electron donor. In H_2O, the green color of the oxygen represents a higher negative charge, corresponding to lower oxidizing but better electron donor ability. In OH^- ion, the blue color of the oxygen corresponds to essentially no residual oxidizing power but good electron donor ability. The hydrogen atoms in these models differ from small red-orange in H_3O^+ ion to larger orange in H_2O to larger and blue-green in OH^-, indicating in the last a high negative charge. With these models, the general nature of aqueous acids and bases is easily understood, and neutralization whenever H_3O^+ and OH^- come in contact is recognizable as inevitable: the blue hydroxide oxygen is a much better electron donor to a proton than is the green oxygen of water.

Differences between weak and strong aqueous acids, and the corresponding differences in hydrolysis of their salts, are clearly indicated by the new models. The extent of ionization of acids is the complex result of a

number of factors but a rough simplification is possible if it is recognized that acid strength will tend to vary inversely with the ability of the anion from the acid to act as electron donor to a proton. Thus models of the

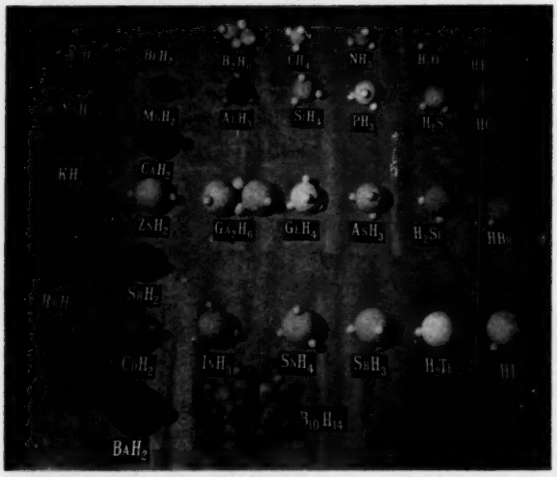

Figure 4. Some binary hydrogen compounds.

carbonate and phosphate ions show the oxygen as blue and highly negative, corresponding to the ease with which it can donate electrons to a proton and therefore to the weakness of the free acid and the susceptibility of carbonates and phosphates to hydrolysis. In contrast, the oxygen atoms in models of the nitrate and perchlorate ions are medium or yellowish-green, displaying only a relatively small negative charge on oxygen with greatly reduced capacity to donate electrons to protons. This is consistent with the well-known strength of aqueous nitric and perchloric acids and the absence of hydrolysis of their anions in solutions of their salts. Models of acetic acid, trichloroacetic acid, trifluoroacetic acid, and their anions are aptly illustrative of the same general principles; the oxygen in acetate ion, for example, being greenish-blue compared to yellowish-green in the trifluoroacetate ion.

From the models, the oxidizing power of acids and water toward active metals can be seen to come not only from the positive hydrogen but also from the fact that the oxygen is not very negative. While in the dissolution of a metal, some of the hydrogen is being reduced to zero charge in forming the free element, the remaining hydrogen and oxygen are also being reduced, either to less positive hydrogen and more negative oxygen in water, or to negative hydrogen and very negative oxygen in hydroxide ion. In general, the close relationship between acid properties and oxidizing power, and between basic properties and reducing power, is clearly shown by such models. For instance, it is easy to see why hydroxide ion is a stronger electron donor than is water.

Models of all the oxides of the nonmetals will show the oxygen to have been relatively unsuccessful, to varying degrees, in acquiring negative charge; oxygen atoms in these models will all be of some yellow-green hue. This is consistent with the oxidizing powers of these compounds, exhibited in many reactions in which the oxygen readily leaves them to unite with some other element from which it can gain higher negative charge. It is also consistent with the acidic properties of such oxides since attraction for electrons causes them to unite readily with compounds of highly negative oxygen which can act as electron donor toward them. This is, of course, the familiar reaction between acidic and basic oxides to form complex oxide salts.

Similarly, models of all the oxides of the active metals will show the oxygen to be blue or greenish-blue, indicating that these compounds are not oxidizing agents under normal circumstances and that they can serve as Lewis bases, the oxygen acting as electron donor. In the reaction of such oxides with water to form basic hydroxides, the oxide oxygen is donating a pair of electrons to a proton from the water. In the reaction of water with acidic oxides, on the other hand, the water oxygen is acting as electron donor to the acidic oxide. The intermediate condition of the oxygen in water is what makes possible this twofold functioning and contributes so greatly to the chemical importance of water.

Hydrogen and Its Binary and Complex Compounds. The intermediate condition of the oxygen in water just mentioned is, of course, the consequence of the intermediate electronegativity of hydrogen. Hydrogen can readily act either as oxidizing agent or reducing agent. One can predict that its oxidizing ability along with its electron-accepting ability should increase as it acquires positive charge, and its reducing ability should increase, along with its electron-donating ability, as it acquires negative charge. Figure 4 is a photograph of some models of binary hydrogen compounds. Such models show very vividly the condition of the combined hydrogen, which is easily recognizable as being remarkably consistent with the properties of the compounds. For example, it is well known that lithium hydride forms ionic crystals, reacts vigorously with compounds of positive hydrogen liberating hydrogen gas, and forms complex hydrides in which its hydrogen acts as electron donor. These properties correspond in a model to a greenish-blue color for the hydrogen, representing its high negative charge. Hydrogen has a similar appearance in all compounds having similar properties, which include the other alkali metal and alkaline earth metal hydrides. The hydrogen in the model of beryllium hydride is still quite negative as indicated by the green color, but appreciably less so. Its general physical and chemical properties are similar. In diborane, B_2H_6, the hydrogen is now only slightly negative, as indicated by the greenish-yellow color. Here the physical association is limited to dimerization, but the compound is still capable of reacting with positive hydrogen compounds, yielding hydrogen gas, although its hydrogen is too slightly negative to serve as electron donor except perhaps in the "hydridic bridge" dimerization. In methane, the hydrogen is slightly positive but so slightly that the color in the model is yellow, indicating neutrality, with the carbon yellow-green indicating slight negative charge. Here are lost all tendencies to associate or serve as electron donor, or to react easily with compounds of positive hydrogen. Then with ammonia, the positive charge on hydrogen shows up as an orange color, consistent with its small ability to act as an acid and its tendency toward "protonic bridge" association through formation of hydrogen bonds. In water, the hydrogen is a redder orange, consistent with its greater acidity, oxidizing power, protonic bridge strength, and acidity in this

series of compounds. Hydrogen fluoride carries the trend one more step. In summary, the change in the nature of binary compounds of hydrogen across the periodic table is very clearly displayed by the new models.

Association of hydrogen compounds appears possible either through ionic or "hydridic bridge" bonding when the hydrogen has negative charge or through "protonic bridge" bonding when the hydrogen has positive charge and the negatively charged atom is small. The "anomalous" properties of ammonia, water, and hydrogen fluoride compared with their respective congeners are easily explained by the models, which show these first members of the group not only to possess hydrogen of higher positive charge but also to have the smaller and more negative atoms, permitting a closer and stronger association through hydrogen. The formation of complex hydrides such as the borohydrides and the aluminohydrides can be seen from the models to involve coordination of a BH_3 or an AlH_3 group only with a more negative hydrogen of some other hydride, in general giving greater stability the more negative the hydrogen of the other hydride and the lower the polarizing power of the metal. The models indicate why borohydrides or aluminohydrides of such elements as carbon and phosphorus are not known.

Binary Compounds of Chlorine. Models of the binary compounds of chlorine, some of which appear in Figure 5, show very clearly the trend in the condition of combined chlorine from very negative in NaCl to neutral in Cl_2. The chlorine in NaCl is of course blue, and it ranges from blue-green in $MgCl_2$ and green in Al_2Cl_6 to yellow-green in $SiCl_4$ and PCl_3 and greenish yellow in SCl_2. This change in condition is concurrent with the change in physical properties from solid salt through molecular or only slightly ionic crystal to volatile liquid and gas. In chemical properties, the change is from relatively inert, except for electron donor ability, toward increasing oxidizing power and increased susceptibility to hydrolysis. In hydrolysis, the combined chlorine atom becomes chloride ion, thus increasing its negative charge to a maximum. Although the potential chlorinating power of combined chlorine when its negative charge is relatively low is not always appreciated, the models show clearly why it should not be overlooked. For example, carbon tetrachloride is generally regarded as quite inert, but the model shows that the chlorine, pale yellow-green, is only slightly negative and potentially a strong chlorinating agent. Mixed with an active metal, such as aluminum, carbon tetrachloride may show no tendence to react, but if reaction happens to be initiated, it may be disastrously explosive. Again this emphasizes the general principle that a highly electronegative element such as chlorine will tend to abandon its position in combination if a greater negative charge can be acquired by the change. The model of Al_2Cl_6 shows by the green color of chlorine a substantially higher negative charge than in CCl_4.

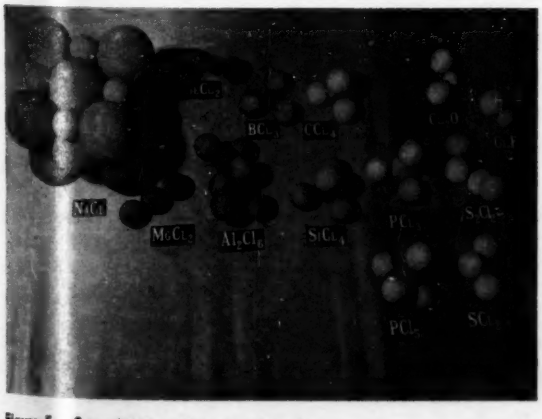

Figure 5. Some binary chlorine compounds.

Figure 6. Proposed initial set of models for general chemistry teaching.

Models for Teaching General Chemistry

Any teacher could find good use for a hundred or more models, but it is possible to construct a set of only 25 which can illustrate most of the principles of elementary chemistry. Figure 6 shows this initial set, which can be helpful in teaching the following:

(1) Relative sizes of atoms and ions and the distinctions between elements and compounds.

(2) The nature of bonds: ionic, polar covalent, nonpolar covalent, coordinate covalent, single, and multiple.

(3) The relationship of bond polarity and structure to molecular polarity. For example, the bonds in CO_2 are polar as shown by the green oxygens and the orange carbon, but are symmetrically directed, making the molecule nonpolar. In H_2O, on the other hand, the bonds are also shown as polar but being unsymmetrically directed they impart polarity to the molecule.

(4) The relationship of molecular structure to the conditions under which a compound or element is solid, liquid, or gas.

(5) Reactants and products in chemical reactions. At least 21 different chemical equations can be represented by the models of this set, making the meaning of such equations much clearer to beginning students.

(6) The nature of water, aqueous acids, and bases, and the hydrolysis of salts.

(7) Oxidation-reduction and oxidation state. For example, the sulfur atom in a model of H_2S is yellow-green (negative), but in a model of H_2SO_4 it is orange (positive). The yellow (neutral) H_2 molecule can be described as reacting with the yellow (neutral) Cl_2 molecule yielding HCl in which the hydrogen has become oxidized (orange, positive) and the chlorine has become reduced (green, negative).

(8) Introducing organic chemistry. The model of CH_4 illustrates the simplest of organic compounds. Together with the model of the chlorine molecule and that of HCl, it can be used to show how derivatives of methane can be made by successive substitution for hydrogen atoms, with CCl_4 the final product along with HCl. The model of acetic acid shows the result of removing one hydrogen atom from methane and replacing it by a carboxyl group.

There is almost no limit to the application of these models to teaching chemistry, at all levels. Despite advances made in recent years, instruction in inorganic chemistry still needs much closer integration of explanatory with descriptive material. It is hoped that models such as those described herein will be found generally helpful in this direction.

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Graduate level laboratory course

Techniques in Inorganic Chemistry

Many first-year graduate courses in laboratory techniques in inorganic chemistry are inadequate and frequently do not achieve the objectives proposed for them. This is especially true of the so-called "preparations" courses, which often degenerate into little more than a modification of "cook-book" chemistry.

One major objective of this type of course is to help students obtain a reasonable degree of competence in certain fundamental laboratory operations along with an understanding of the nature and appropriate uses of these operations. Frequently laboratory preparations courses are designed with the hope that, in carrying out the assigned experiments, the students will gain the desired understanding and manipulative competence automatically, as if by some mystical transfer. That this occurs to any large extent is open to serious question.

It is proposed that if it is desirable for students to learn a particular laboratory technique or manipulation, the particular technique *itself* be taught in the laboratory, and that laboratory preparations be used only as illustrative material. Consequently, it becomes necessary to delineate carefully the important techniques which should be included in a first-year graduate course. An effort should be made to avoid unnecessary duplication of techniques which will be presented in other laboratory courses, either within inorganic chemistry or in other areas.

An outline of the techniques currently under study for inclusion in the first-year graduate course in laboratory techniques in inorganic chemistry at Wayne State University is given below. Some of these have already been incorporated into the existing course with considerable success and it is expected that others will soon be included. The concept of teaching *the technique itself* and using *illustrative* preparations has proved superior to the previous concept of a course in laboratory preparations. Some evidence for this at Wayne is found in the markedly decreasing use of the professional glassblower employed by the University within the last five years, although the number of graduate students and staff engaged in research activities has increased substantially during the same period. Furthermore, there has been a noticeable increase in the research investigations which involve use of many of the techniques described below, apparently at the expense of some test tube research.

In practice, a lecture-demonstration is given to the class on the technique under discussion, after which the students are assigned laboratory preparations which involve this technique and probably others as well. It is the responsibility of the student to locate a suitable experimental procedure in the literature, to construct the necessary apparatus, and to carry out the preparation. Students are expected to work alone although they are encouraged to solicit *advice* from the instructor and more advanced students. Each student performs between eight and ten preparations per semester and reports orally on about six of them. The oral report takes approximately 20 minutes and is concerned primarily with the important aspects of the experimental procedures. The student is questioned during the presentation by the instructor as well as other members of the class. A written report outlining the important experimental techniques is turned in by the student along with the sample of the substance prepared, usually at the time of the oral presentation. The average number of students in a class is about ten and the class usually meets formally for two recitation-lecture hours per week. The average time spent in the laboratory is between eight and 12 hours per week, although students may spend more time on these preparations at their research desks if they desire.

Students are expected to consult journals of original research as well as books in order to find suitable preparative procedures for their assignments. Among the books used are the *Inorganic Syntheses* series, *Handbuch der praparativen anorganischen Chemie* by

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Brauer, *Experimental Inorganic Chemistry* by Dodd and Robinson, and *Experimental Inorganic Chemistry* by Palmer. In addition, books on special phases of laboratory techniques are used as supplementary reading sources (e.g., *Laboratory Glassworking for Scientists* by Robertson, *et al.*, and *Vacuum Manipulation of Volatile Compounds* by Sanderson).

The compounds chosen as assigned preparations vary from semester to semester and cost of chemicals and materials is sometimes a factor in the choice. One part of the laboratory is equipped with special apparatus such as ovens, muffle furnaces, balances, a refrigerator, a centrifuge, a shaker, a pulverizer, d.c. electricity, vacuum pumps, glassblowing equipment, etc.; and, with time, cost has become less important as a factor in the assignment of preparations.

Techniques are chosen from the following list and a student comes in contact with about a fourth of these during a semester:

Manipulation of pure substances
Weight: special weighing apparatus
Temperature: measurement and control
Environment: desiccants, active and inert atmospheres

Properties of pure substances
Measurements: changes of state, density, magnetic susceptibility
Separations: distillation, sublimation, precipitation, coagulation, crystallization, filtration, optical resolutions, extraction, ion exchange, chromatography

Manipulation of laboratory apparatus
Glassworking, low and high pressure techniques, electrical measurements, grinding and pulverizing, mixing

Special techniques in inorganic chemistry
Electrolytic preparations, non-aqueous solvents, fused salts, stability constant determinations, large crystals, coordination compounds, anhydrous halides, mineral extractions, alloys, organo-metallic compounds, inorganic polymers, catalysis

Manipulation of radioactive materials
Detection and measurement of radioactivity, safe handling procedures, preparative methods, tracer techniques

Safety in the chemical laboratory
Safety equipment, accident prevention, explosions and fires, safe handling of electricity and toxic substances, laboratory first-aid

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A New Course in Synthetic Inorganic Chemistry

The paucity of synthetic inorganic chemists in the United States is surely not caused by a lack of inherent talent, but rather by an educational system which tends to create the illusion that there are no new kinds of compounds to be discovered. Therefore, at Berkeley, we teach a course the primary purpose of which is to awaken synthetic talents in students. This course in synthetic inorganic chemistry is a one-semester, three-unit course, consisting of one hour of lecture and six hours of laboratory work per week.

In the lectures, an attempt is made to show the students "how synthetic chemists think." First we examine the various motivations of synthetic chemists—both those who prepare new compounds and those who find new methods for preparing already known compounds. Such considerations may seem trivial, but it must be remembered that the average undergraduate student has not yet engaged in pure research and has not enjoyed the thrill of original discovery.

Accidental Discovery. Simple chance, coupled with astute observation, has been responsible for the discovery of many new compounds. Oftentimes in the course of what is thought to be a straightforward synthesis or investigation, something completely unexpected happens. Perhaps an unexpected precipitate forms, a gas is evolved, a reaction mixture turns an unusual color, or a yield of expected product is very low. Unfortunately, the average chemist usually ignores such phenomena and goes on to work which he can understand. But the curious chemist tries to find out what "went wrong" and, in the process, usually makes a significant discovery, sometimes a spectacular discovery.

For an example of this type of discovery, one may cite the attempt of Kealy and Pauson[1] to make dihydrofulvalene (a hydrocarbon containing two five-member rings) by the oxidation of cyclopentadienylmagnesium bromide with ferric chloride. They found none of the desired product, but they did isolate a remarkably stable organo-iron compound which they identified as biscyclopentadienyl iron ("ferrocene").[2] Today this compound and other transition-metal "sandwich" compounds hold the attention of many inorganic chemists.

In the laboratory, it is important that the instructor insist that the students be on the alert for unusual happenings. An attempt should be made to understand all phenomena. Indeed, students may learn as much from unsuccessful experiments as from successful ones.

Presented as part of the Symposium on Instruction in Inorganic Chemistry, sponsored jointly by the Divisions of Chemical Education and Inorganic Chemistry at the 134th meeting of the American Chemical Society, Chicago, Illinois, September, 1958. For other papers in this series see THIS JOURNAL, 36, 441 (1959).

[1] KEALY, T. J., and PAUSON, P. L., *Nature*, 168, 1039 (1951).
[2] For a review of the chemistry of ferrocene see RAUSCH, M., ET AL., THIS JOURNAL, 34, 268 (1957).

Curiosity. Most creative scientists are motivated by curiosity. Curiosity led Alfred Stock to the discovery of an entirely new class of compounds: the boron hydrides and their derivatives. Stock[3] stated that in 1912 he chose to study the boron hydrides because he felt that boron, the neighbor of carbon in the periodic system, might be expected to form a much greater variety of interesting compounds than merely boric acid and the borates, which were almost the only ones known at that time. But he probably never dreamed that, in the next 20 years, he and his coworkers would prepare such an extensive and fascinating series of compounds as are described in his monograph, "Hydrides of Boron and Silicon."

We try to spark the curiosities of the students by describing current research and by encouraging students to prepare unusual, "exotic" compounds.

Testing Theories. There are innumerable examples of compounds which were prepared for the first time in order to test the validity of a theory. Most of the complex compounds prepared by Alfred Werner were prepared in order to build up confirming evidence for his famous coordination theory.

Discovery to Fulfill a Need. New compounds are often prepared because of an urgent need for them. During World War II, a great deal of effort was expended in an attempt to find volatile uranium compounds which could be used in isotopic separation processes. This work led to the discovery of many fascinating uranium chelates and miscellaneous borohydrides. Nowadays, chemists are tailor-making new kinds of refractories and high-energy fuels for use in rockets.

New Methods for Preparing Old Compounds. The synthetic chemist is not only concerned with the preparation of new compounds—he often seeks new and better methods for preparing compounds which have been known for many years. Usually the first method used for the preparation of a compound is inefficient or inconvenient. Thus the motive for seeking a better synthetic procedure is obvious. There are many inorganic compounds which would change from "laboratory curiosities" to commercially important chemicals if practical syntheses were found for them. For example, the compounds B_2Cl_4 and N_4S_4 particularly challenge chemists' ingenuities.

Thermodynamics and Kinetics. It is important that students appreciate the importance of thermodynamics and kinetics in synthesis.[4] As an example of thermodynamic reasoning, consider a chemist who is wondering whether or not he can make hydrazine by the oxidation of aqueous ammonia by nitric oxide. By reference to a table of free energies, he would quickly calculate that $\Delta F^\circ = 48.9$ kcal/mole at 25° for the reaction

$$8NH_3 + 2NO = 5N_2H_4 + 2H_2O$$

and know that, under ordinary conditions, the method would not work. Kinetic considerations are frequently of importance in synthetic work. As a simple example, we may cite the preparation of lithium hydride. Although the reaction of lithium and hydrogen to form lithium hydride is thermodynamically favored at room temperature, there is no appreciable reaction until the reactants are heated to about 700°.

[3] Stock, A., "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

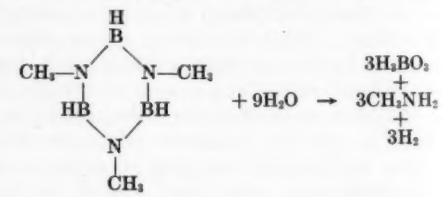
[4] See other papers in this symposium, notably that by Taube, H., this Journal, 36, 451 (1959).

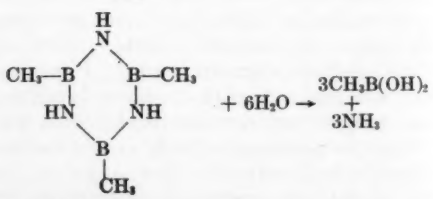
Table 1. Types of Compounds

Type	Examples
Strong oxidizing agent	K_2FeO_4, SO_4
Strong reducing agent	KNH_2, LiH
Coordination compound	$[Co\ en_2Cl_2]Cl$, $K_2Ni(CN)_4 \cdot H_2O$
Organo-Metallic compound	$Fe(C_5H_5)_2$, $Pb(C_6H_5)_4$
Volatile halide	$VOCl_3$, $AsCl_3$
Polymer	$(NaPO_3)_x$, $(PNCl_2)_x$
Volatile hydride	PH_3, B_2H_6
Miscellaneous gas	COS, HCOF
Metal	Ge, B
Intermetallic compound	Na_4Pb_9, $NaSn_2$
"Sub"-compound	Ag_2F, Cs_7O_2
Miscellaneous	Li_3N, S_4N_4

Acid-Base Concepts. Since many inorganic reactions may be thought of as acid-base reactions, it is important that students be aware of the various generalized acid-base concepts, including the protonic concept, the solvent concept, and the Lewis concept. After covering these ideas, it is easy to discuss topics such as syntheses in liquid ammonia, the synthesis of coordination compounds, and the synthesis of complex hydrides.

Structure from Chemical Data. In most of our other undergraduate courses, students learn how various physical properties may be related to molecular structure. In this course, we spend some time discussing the relationship between *chemical* behavior and structure. This is a topic which is familiar to organic chemists, and we feel that inorganic chemists can profit from such considerations. For example, we would expect students to be able to distinguish N,N,N-trimethylborazine from B,B,B-trimethylborazine from the amount of hydrogen evolved upon hydrolysis.





Laboratory Work

The laboratory work has two main purposes: (1) to familiarize the students with a wide variety of compound types, including some which they probably do not realize exist (it is hoped that this will cause some students to wonder about unknown compounds), and (2) to teach the students the important experimental techniques which are available for synthetic work.

Each student is required to prepare six different compounds. The students themselves choose which compounds they make, but they are restricted to the extent that each compound must be of a different "type" (as listed in Table 1) and that, during the semester,

Table 2. Special Techniques

1.	Electrolytic oxidation or reduction
2.	High temperature process (resistance furnace) involving controlled atmosphere
3.	High temperature process (resistance furnace) not involving controlled atmosphere
4.	Use of non-aqueous solvent
5.	Use of electric discharge
6.	Use of ion-exchange column
7.	Use of high-pressure apparatus
8.	Fractional or continuous extraction
9.	Use of inert-atmosphere box
10.	Vacuum manipulation

they must use at least six of the "special techniques" listed in Table 2. Occasionally we find it necessary to disallow a student's choice of synthesis. This is usually done because the synthesis is too dangerous or too difficult; students seldom choose trivial syntheses. It will be noted that the first eight techniques of Table 2 require equipment which is available, or readily assembled, in most college chemistry departments. The inert-atmosphere box may be a problem for some schools. In this respect it should be mentioned that a large transparent polyethylene bag, flushed with argon, serves as a convenient substitute for an inert-atmosphere box. A thin-walled bag offers little impediment to manipulation and is very impervious to moisture. The glass parts for a vacuum line might easily cost $300, but the maintenance costs are relatively small.

The students are furnished with directions for the use of the special equipment, but they are not furnished with directions for the preparation of their chosen compounds. They go to the literature for their synthetic methods. They are asked to attempt improvement of literature methods with respect to one or more of the following points: (1) simplicity of procedure, (2) purity of product, (3) percentage yield of product, and (4) cost of product. The purity of the six products must be evaluated by quantitative or semiquantitative analyses. In many cases, sharpness of melting point or boiling point is an acceptable criterion of purity. In other cases, qualitative analyses for the more likely impurities may suffice. In cases where simple criteria such as these are impossible, a simple quantitative analysis (preferably volumetric) may be necessary.

In addition to the six required syntheses, each student is required to perform an analysis using the vacuum line. He may choose either to determine the equivalent weight of an "unknown" acid in liquid ammonia by measuring the hydrogen evolved when the acid reacts with sodium or to analyze qualitatively an "unknown" mixture of volatile materials. Students must complete this assignment before they use the vacuum line for purposes of synthesis.

During the last three weeks of the semester, the students work on a minor research problem which involves either the preparation of an entirely new compound or a new synthetic method for a known compound. The results of this research are written up in the style of a typical article from the *Journal of the American Chemical Society*.

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Inorganic Chemistry Taught as a Requirement for All Professional Chemists

One objective of the symposium of which this paper is a part is to discuss methods and course content for the teaching of inorganic chemistry. Much attention has been given to the teaching of inorganic chemistry to the student interested in specializing in this field—this is indeed an important aspect of the situation. It is perhaps of even more importance, however, to consider the need for the teaching of inorganic chemistry as an essential part of the training of every professional chemist, for it is the strong belief of the author that inorganic chemistry provides an important area of study, offering unique values, in the training of chemists for a great variety of special fields far beyond the bounds of what is normally considered the professional area of operation of inorganic chemists. The teaching of a properly designed course in inorganic chemistry to all chemistry graduate students and undergraduate chemistry majors is an exceedingly important consideration in the development of a modern and effective system of chemical education.

Presented as part of a symposium on Instruction in Inorganic Chemistry, sponsored jointly by the Divisions of Chemical Education and Inorganic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958. For other papers in this series see THIS JOURNAL, 36, 441 (1959).

Essential to the Understanding of Modern Chemical Theory

The reason for the importance of inorganic chemistry to chemical education lies in the paths which the development of chemistry as a science has taken during the past half century. During this period, the field of chemistry has changed from an empirical science, emphasizing descriptive aspects of the subject, to a science in which ever increasing attention is given to the correlation of theory and fact—a science in which a dependable theoretical structure in terms of which the properties of matter can be understood and predicted is rapidly being developed. The characteristic which most clearly distinguishes the chemist of today from his counterpart of 50 years ago is the awareness of a

system of theoretical concepts concerning the structures of atoms, molecules, ions, crystals, and other aggregates of matter—a system which he can use as a guide to his research and as a basis for the prediction of the properties of new substances as yet "unborn." It is, therefore, inconceivable that any college or university which seeks to train chemists properly should ignore or fail to emphasize properly the need for assuring the training of its students in these most important structural concepts.

If the student is to achieve the desired degree of understanding of the structural theory of modern chemistry, he must have the opportunity to consider the manner in which the properties of systems change as the various atomic parameters change over a broad range—the kind of range which is available if all the elements (the entire periodic system) are brought into consideration; in other words, he must have the opportunity to study modern inorganic chemistry at an intellectually sophisticated level.

Let us consider a few examples of important theoretical concepts which require, for broad understanding, a proper training in inorganic chemistry, and which can best be taught within the context of such a course.

Relationship of Properties to Bond Type and Structure

This is the most fundamental topic of modern chemistry. It requires a knowledge of atomic structure (particularly electronic configurations) and a knowledge of the variation of such properties as ionic and atomic radii, ionization energy, electronegativity, and electron affinity with changes in atomic structure. This can be learned most effectively from a study of the periodic system as a whole.

It is desirable, furthermore, that the student have a broad understanding of interatomic forces, including not only ordinary ionic and simple covalent bonds but also various delocalized bonds such as metallic bonds, three-center bonds, and other more esoteric varieties. The student should also know the conditions under which each type of bond is to be expected and, further, the kinds of properties which are associated with each type of bonding. It is in the study of inorganic chemistry that a broad treatment of this topic can most efficiently and naturally be presented.

Multiple Bonding

It might be considered that the concept of multiple bonds could be adequately treated in terms of the content of organic chemistry and would not require the broader treatment available when all the elements are considered. However, although the study of carbon compounds contributes much to our understanding, it is only when we expand our field that the real significance of multiple bonding appears. Why, for example, does silicon dioxide have such different physical properties from those of carbon dioxide? Why are the ketones monomeric, whereas the silicones polymerize? Why does elemental nitrogen form very inert N_2 molecules, whereas phosphorus and arsenic form the much more reactive P_4 and As_4 molecules? The answers to these and other such questions lie in the fact that *pi* bonding involving *p*-orbitals occurs much more readily with first-row elements than with other elements in the periodic system. On the other hand, many phenomena involving second and lower row elements may be explained in terms of *pi* bonding involving *d*-orbitals. For example, after having been given the fairly common but too superficial explanation that the difference in polymerization properties of silicones and ketones results from the lack of ability of silicon to form double bonds, the chemist encounters the experimental fact that whereas trimethylamine is a basic, pyramidal molecule, trisilylamine is an almost non-basic, planar molecule. He then learns that silicon *does* form *pi* bonds but that these *pi* bonds utilize *d*-orbitals of the silicon atom and thus do not reduce its covalence nor destroy its tetrahedral configuration. The nitrogen atom in trisilylamine, however, goes over to sp^2 hybridization and becomes planar. This is not an isolated example. It is in the study of the phenomenon of multiple-bond formation against the broad background of inorganic chemistry that the chemist becomes aware of the many parameters which are relevant to this phenomenon.

Molecular Addition Compounds—Coordination Theory

One of the most interesting developments in chemistry during the past half-century has been the discovery of the great role played by molecular addition compounds and by metal ion-coordination complexes in chemical phenomena, and of the development of coordination theory and the Lewis acid-base theory to explain these phenomena. Whereas many examples of molecular addition compounds can be found in the realm of organic chemistry, they cover a relatively narrow field as compared to those found in the chemistry of such inorganic substances as chromium(VI) oxide, sulfur trioxide, dinitrogen tetroxide, tin tetrachloride, boron trifluoride, aluminum chloride, and many others. The field of metal-coordination complexes is, of course, almost entirely within the scope of inorganic chemistry. Principles learned in the comparative chemistries of analogous nitrogen and phosphorus molecular addition compounds and the contrasting behavior of analogous silicon and carbon compounds toward electron donors have been of much significance in various areas of organic chemistry.

Stereoisomerism

The study of stereoisomerism has been so completely associated in our undergraduate curriculum with the field of organic chemistry that many of our students would answer as a student I heard once, who, when asked what optical isomers are replied that they are "isomeric forms of compounds containing asymmetric carbon atoms." A similar limited outlook is often found among our students with respect to geometric or *cis-trans* isomerism. Yet the field of stereoisomerism may be approached in a much more general and more logical way when metal complexes, and compounds of phosphorus, beryllium, boron, sulfur, silicon, tin, and nitrogen, are considered along with carbon compounds. Such an approach leads to a much greater variety of examples as well as to a broader understanding of the principles of stereoisomerism than can readily be achieved through the study of organic chemistry alone. The stereoisomeric possibilities of the octahedral chelate

complexes are considerably more varied than those of the tetrahedral carbon atom and add much insight to the study of isomerism as related to molecular symmetry.

Acid-Base Theory

If the student is limited to systems normally considered in organic chemistry, his understanding of the broader concepts of acidity and basicity will be severely limited. The study of chemistry in such solvents as hydrogen fluoride, ammonia, dinitrogen tetroxide, anhydrous sulfuric acid, liquid sulfur dioxide; the study of fused salt systems; and the study of high-temperature interactions in refractory oxide systems all make a major contribution in this area, and these topics are generally covered principally in inorganic chemistry.

A very large number of organic reactions proceed by acid-base type mechanisms which require that the informed organic chemist possess a rather high degree of sophistication in the use of the Brønsted-Lowry and the Lewis concepts of acidity and basicity. Examples include Friedel-Craft reactions, nitrations of aromatic compounds in nitromethane, halogenation of double bonds, Grignard reactions, hydration of olefins, Claissen condensations, and many others.

The above topics are only a few examples. To these examples of concepts to which the study of inorganic chemistry is especially valuable we might add many others such as electrochemical processes, oxidation potentials, the concept of resonance, and magnetic properties of substances.

Source of Essential Factual Information

Apart from the usefulness of inorganic chemistry as the most efficient milieu for teaching modern theoretical concepts, the need for training in inorganic chemistry as a means of providing essential working information to support present day research in the various fields of chemistry needs emphasis.

Consider, for example, the tremendous amount of work being done in the areas of boron, silicon, and phosphorus-organic compounds, not to mention the strong research effort being directed toward developing the field of metal-organics. The weakness in background in inorganic chemistry of many organic chemists working in this area is well illustrated by the rather trivial error, in itself, of considering boron, silicon, and phosphorus alkyls as metalloorganic compounds. A thorough knowledge of the periodic system as it is related to atomic structure would prevent such misconceptions and would, without doubt, accelerate research progress in this field.

The past few years have seen the addition of many new reagents and solvents to the arsenal of the synthetic organic chemist. A surprisingly large number of these new reagents and solvents are inorganic compounds and have been developed by inorganic chemists. Examples include the phosphotungstates, the alkyl borohydrides and the alkyl aluminum hydrides, nitryl chloride, the N_2O_4—BF_3 complex, and dinitrogen tetroxide, as well as the many metal and non-metal fluorides being used in fluorine organic chemistry.

Broader training in modern inorganic chemistry is also demanded as a result of developments in the area of nuclear science. Nuclear power development demands new metals such as zirconium and hafnium. Atomic fission-product separation and the utilization of radioisotopes in widely diverse applied and theoretical researches require a detailed knowledge of the chemistries of elements which were only laboratory curiosities a few years ago. The effects of high-intensity radiation on structural materials have also placed a premium on knowledge of the properties of metals and other solids.

Interest in new metals such as titanium and germanium has also served to increase the need for chemists with inorganic training.

The development of jet and rocket engines for military and, more recently, civil aviation has provided a tremendous stimulus to the search for materials which retain their strength at elevated temperatures. Associated with the trends toward higher and higher operating temperatures for these engines is the search for high-temperature lubricants and for materials which will be stable at high temperatures and yet will be flexible. Most striking, however, has been the tremendous impact on chemistry of developments in the rocket-missile-satellite program. Here the chemist is under pressure to produce fuels of higher and higher energies. The need for higher and higher specific impulses and the fact that relatively small increases in specific impulse make possible a tremendous increase in range of a rocket-launched missile lead to the consideration of some very unusual and rather bizarre systems as possible fuels and oxidizers. Major areas of study in this field rest largely on inorganic chemistry. Hydrazines, hydroborons, oxides of nitrogen, perchloryl fluoride, and other fluorine compounds—all these and many others are now very "practical" considerations in rocket chemistry.

Inorganic Chemistry Must Be Modern

One may not, therefore, escape the conclusion that all chemists of today must be adequately trained in modern inorganic chemistry, but the word *modern* must receive strong emphasis. We cannot expect to fulfill this need with old-fashioned, principally descriptive, courses in inorganic chemistry, the dullness of which was, as a matter of fact, largely responsible for the near-demise of inorganic chemistry in our colleges only a few decades ago. Our courses must be systematic, i.e., must show systematic correlation of fact with theory so that the student will see in the subject matter of inorganic chemistry a broad demonstration and exemplification of the principles of theoretical chemistry. By applying these principles, the properly trained inorganic chemist will be able to use the rich and varied resources of the periodic system to develop new ideas and to synthesize new substances to meet many of the scientific demands of our day.

A Suggested Program

There is, of course a variety of programs which will help to achieve this objective. The program followed for professional chemistry majors at the University of Florida includes in the senior year (after the standard physical chemistry course in the junior year) one semester of theoretical chemistry and one semester of systematic inorganic chemistry, including three to six

hours per week of inorganic laboratory work. All beginning graduate students are required to take one semester of introduction to modern theoretical chemistry followed by an intensive one-semester course in structural inorganic chemistry. This is then followed, for those who desire further work or who will specialize in inorganic chemistry, by a one-year course in systematic (by periodic families) inorganic chemistry at a highly sophisticated level. In addition, one semester of advanced inorganic laboratory work and various special-topics seminars are offered.

In order to illustrate the type of training toward which we are striving, the following outline of the course in structural inorganic chemistry which is given to all graduate students at the University of Florida is included:

Review of Atomic Structure
- Quantum numbers an l orbitals as related to the wave nature of matter.
- Electronic configurations of the elements. The penetration effect. The "building-up" principle.
- Variation in atomic parameters with position in the periodic system. Relation of these parameters to bond type, acidity and basicity, complex formation, coordination number, and similar topics.

Bonding Forces Between Atoms
- The covalent bond
  - The valence bond treatment—Review.
  - Molecular orbital treatment. σ and π bonding.
  - Comparison of "valence-bond" and "molecular orbital" methods.
- The ionic bond
  - Summary of various types of crystalline solids—ionic, molecular, atomic, and metallic.
  - Derivation of equation for the lattice energy of an ionic crystal. The Madelung constant.
  - Ionic radii—derivation and applications.
  - Some simple ionic structures.
  - Structural principles in complex ionic crystals.
  - A chart of crystal types based on internal packing.
- Metallic crystals
  - Nature of the metallic state. The fundamental theoretical problem.
  - Bloch's molecular oribital method.
  - Pauling's atomic orbital method.
  - Comparison of Bloch and Pauling methods.
  - Intermetallic systems.
- Interstitial compounds. The refractory carbides, borides, and nitrides.
- Non-stoichiometric phases.

Complex Compounds
- Survey of the phenomena of complex formation.
- Experimental methods for studying complex compounds.
- The nature of bonding in complex compounds.
  - The valence-bond approach.
  - Molecular orbital theory of complexes.
  - The electrostatic theory of coordination compounds as modified by crystal field theory.
  - Comparison of the three approaches.
- Stereochemistry of complex compounds. Isomerism.
- Applications of the theory of complex formation to the understanding of a variety of reactions.
- Molecular addition compounds.

It is with this background that graduate students specializing in inorganic chemistry begin a one-year study of the chemistry of the elements based upon the periodic system and using the most modern structural concepts for the understanding and correlation of experimental information.

Literature

Because of the relative scarcity of textual materials in the field of modern inorganic chemistry, it will perhaps be of interest to briefly indicate the principal reference materials for the structural inorganic course outlined above. These are as follows:

Major textual references:

"Structural Inorganic Chemistry"—Wells, 2nd edition. This is an excellent survey of the structures of the principal inorganic solids with particular emphasis on the hydrides, halides, oxides, sulfides, nitrides, and phosphides.

"Valence"—Coulson. A modern treatment of chemical bonding of intermediate difficulty. Suitable for advanced undergraduate and graduate students.

"Valency and Molecular Structure"—Cartmell & Fowles. A treatment of modern concepts of chemical bonding. Contains an excellent qualitative introduction to the molecular orbital concept and also some very interesting structural problems in the various families of the periodic system.

"Modern Aspects of Inorganic Chemistry"—Emeleus and Anderson. 2nd edition. A treatment of several special topics in inorganic chemistry. The treatment of intermetallic phases and non-stoichiometric compounds is particularly useful.

"Mechanism of Inorganic Reactions"—Basolo and Pearson. The chapter on the Theory of the Coordinate Bond is the newest and most comprehensive now available. The critique of the several approaches to the nature of the coordinate link is outstanding.

"Inorganic Chemistry"—Moeller. An excellent single-volume text in inorganic chemistry.

"Chemistry of Coordination Compounds"—Bailar. A rich source of information concerning complex compounds.

Additional selected references:

"Chemical Constitution"—Ketelaar.
"Treatise on Inorganic Chemistry," vols. I & II—Remy.
"Textbook of Inorganic Chemistry," vols. I & II—Sidgwick.
"Oxidation Potentials"—Latimer.
"Electronic Structure & Chemical Binding"—Rice.
"Chemistry of Metal Chelate Compounds"—Martell & Calvin.
"Chemistry of the Actinide Elements"—Katz & Seaborg.
"Quelques Problems de Chimie Minérale"—Institut International de Chimie Solvay.—R. Stoaps, 1956.
"Colloquium of the Section for Inorganic Chemistry"–IUPAC Meeting, 1954.

Journals:

There are, of course, many journals which contain articles of interest to the inorganic chemist. We have, however, found that in addition to the *Journal of the American Chemical Society*, the following journals are particularly desirable:

Journal of the Chemical Society.
Journal of Inorganic and Nuclear Chemistry.
Zeitschrift für anorganische und allgemeine Chemie.
Quarterly Reviews.
Chemical Reviews.
Journal of Chemical Education.

✦ ✦ ✦

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Don Dorotheo Theodoro, First Chemical Technologist of the New World

Many industries have at various times laid claim to the distinction of being the first to be established on this continent or in what is now the continental United States. These claims are usually based on more or less vague allusions in early chronicles and are shrouded in anonymity. It appears, however, that the title of the first chemical technologist of the New World may well be conferred upon Don Dorotheo Theodoro, member of the ill-fated Narvaez expedition of 1527.

Prominent among the claimants for the "first industry" is the Naval Stores Industry. The importance which early explorers and settlers attached to the production of naval stores lends credence to such a claim. Ship captains repeatedly emphasized the potentialities of the New World as a source of naval stores. Pitch and tar were used to calk the seams between the planks of their wooden ships and to waterproof and preserve the cordage and rigging. These products were literally of vital importance not only to the mariners, but to the maritime nations. Pitch and tar were carried as part of the regular ship supplies, were stocked in every seaport, and were known as "naval stores."

"Naval Stores" were obtained by the incomplete combustion (carbonization) of the wood of conifers or from the oleoresinous exudate of wounded pines. The oleoresinous exudate was formerly called crude turpentine, or simply turpentine. Today the latter term is reserved for only the volatile portion of the exudate, the portion formerly known as "spirits" or "spirits of turpentine." Products obtained from the exudate of pines are today still called naval stores even though pitch and tar comprise only a small proportion of these products and their connection with ships is of very minor importance.

Naval Stores in Novia Scotia (1606)

Ostrom (*4*) in his "History of the Gum Naval Stores Industry" states, "Early American naval stores operations began in Nova Scotia in 1606, in Virginia in 1608, and in New England shortly after 1620." This succinct summary is doubtless derived from more detailed accounts in Gamble's "Naval Stores History" (*1*), to which suitable reference is made but which is now out of print and not readily available. Some amplification of this brief summary would seem appropriate.

Gamble states,

> In 1608 eight Dutchmen and Poles were dispatched to Virginia who were to be employed in the manufacture of glass, pitch, tar, soap, etc. When Captain Newport returned to England in the same year, he brought back, as part of his cargo, the accumulation of these commodities which had been provided him. . . . This was the first naval stores shipped from what is now the United States to England, as far as is known.

Gamble acknowledges that two years earlier (i.e., in 1606) the French at Port Royal had "extracted turpentine from the sluggish veins of the Nova Scotia pine," and states

> The French, in probably an amateurish and certainly in a petty way, began what was probably the first naval stores operations in America. Thoreau, that quaint Yankee philosopher who had such a keen observing eye for nature and a vastly retentive memory for all sorts of information gathered from books, tells us in his work on "The Maine Woods" that "when the Pilgrim Fathers were spending their first winter in the New World (1620–21), the French were no further off than Port Royal [Annapolis, N. S.] three hundred miles to the north, where in spite of many vicissitudes they had been for fifteen years." They had built a grist mill and as early as 1606 were making turpentine as Williamson stated in his "History of Maine."

Gamble cautiously observes,

> This may be regarded, in the absence of any more definite information, as establishing the first date at which the American pine gave up its gum for the use of man.

Gamble's caution was warranted since, as will be seen, a distinctly earlier date can be set for such an operation. Gamble observes further,

> What uses those Frenchmen in that lonely settlement put it to one cannot say. It is rather improbable that they produced sufficient to ship to the home country. Even back there it had its medicinal values.

Parkman, in his "Pioneers of France in the New World" (*5*) supplies the answer to Gamble's speculations. Thus he states (p. 276 pertaining to the year 1606),

> Poutrincourt [Baron de Poutrincourt] forgot the prejudices of his noble birth and went himself into the woods to gather turpentine from the pines, which he converted into tar by a process of his own invention.

Thus it appears that the "turpentine" referred to by Thoreau was in reality the crude turpentine or oleoresin and, as Gamble correctly inferred, they did not produce "sufficient to ship to the home country." Parkman refers to still earlier production by the French of what would be called naval stores. Thus he reports (p. 45) that in 1563 the colonists at Port Royal built a brigantine and notes,

> They calked the seams with the long moss which hung in profusion from the neighboring trees; the pines supplied them with pitch.

Naval Stores in Florida (1528)

However, it appears that a still earlier date can be set for the production of naval stores in what is now the

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. The author's present address is: USDA, Western Division, Albany, Calif.

continental United States. The occasion was the production of pitch or tar used in the construction of five crude boats on the shores of Apalachicola Bay, on the Gulf Coast of Florida, in 1528. The story is told by Cabeza de Vaca (literally, the head of a cow), treasurer of the Narvaez expedition and first European to traverse the North American Continent.

A translation of "The Narrative of Alvar Nunez Cabeza de Vaca" which was printed at Valladolid, Spain, in 1555, was prepared by Buckingham Smith and published privately in Washington, D. C., in 1851 (*2*). Another translation (*3*), by Fanny Bandelier, was published in 1905 under the title, "The Journey of Alvar Nunez Cabeza de Vaca and his Companions from Florida to the Pacific 1528–1536."[2]

Fortunately, de Vaca "took care and diligence . . . to keep a particular remembrance of everything."[3] Lost and separated from the ships which took them from Spain, the company undertook to build "some craft in which to leave the land" [Florida]. Despite the lack of tools and materials, and although as he states

> None of us knew how to construct ships . . . we proceeded with so great diligence that on the twentieth day of September [1528, they started on August 4] five boats were finished of twenty-two cubits [thirty-three feet] in length, each calked with the fiber of the palmetto. *We pitched them with a certain resin which was made from pine trees by a Greek named Don Theodoro;* and from the same husk of the palmettos, and from the tails and manes of the horses, we made ropes and rigging, and from our shirts, sails. We flayed the horses, and took off the skins of their legs entire, and tanned them to make bottles in which we might carry water.

Perhaps the tanning industry can now lay claim to being the second, after naval stores, to have begun in what is now the continental United States.

The name of Don Theodoro appears twice more in history. De Vaca reports that the fleet of five boats left on September 22 and after various misadventures as a result of which they "were brought to the last extremity of want" they arrived at an estuary. There, Dorotheo Theodoro chose to go inland with some Indians whom they met rather than continue with the company at sea. Finally, in 1540, some 12 years later, when Hernando deSoto came to the town of Mauvila (near what is now Mobile, Alabama) he found that Don Theodoro had been there and was shown a dagger that he had worn.

Thus, we have the full name of the man who may be the first chemical technologist of the New World. He was a Greek Christian, Don Dorotheo Theodoro by name, who made pitch from pines. He sailed from Spain with the Narvaez expedition in 1527. Separated from the ships that brought them to Florida, to pitch crude boats built in the summer of 1528 near Apalachicola, he made "a certain resin" from pine trees. For a month he and his companions floundered westward in these overloaded boats, beset by storms and tortured by extreme thirst, as the leather bottles they made to hold water soon rotted. Then, somewhere between what are now Panama City and Mobile, Don Theodoro abandoned the expedition, choosing to live among the natives in preference to continuing at sea, and disappeared from white man's eyes. But not without trace. There is evidence that he escaped from the Florida swamps and traveled inland. Perhaps, after all his misadventures with the Narvaez expedition he found his promised land and ended his days, as Buckingham Smith suggests, one of the first European buffalo hunters.

[2] In addition to the two translations, five paraphrases have been published. The latest of these, "Alva Nunez Cabeza de Vaca. The Journey and Route of the First European to Cross the Continent of North America. 1534–1535," by Cleve Hallenbeck, was published by Arthur H. Clark Co., Glendale, Calif., in 1940 (326 pp.). A second edition of Smith's translation, edited by J. G. Shea, appeared in 1871. Hallenbeck states, "This translation has been republished with notes by Hodge in Spanish Explorers in the Southern United States (1907), and was again reprinted, unedited, in 1929." De Vaca's Narrative is considered of importance in stimulating Spanish interest in the unknown lands to the north and was the direct cause of several Spanish expeditions.

[3] All direct quotations of the Narrative are from the translation by Buckingham Smith.

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(3) Nunez (Cabeza de Vaca), Alvar, "The Journey of Alvar Nunez Cabeza de Vaca and His Companions from Florida to the Pacific, 1528–1536," Translation by Fanny Bandelier, Allerton Book Co., New York, 1922 [*c. 1904*], xxii, p. 231.

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An extremely useful purchase guide has been prepared by a selected committee of scientists and educators for the Council of Chief State School Officers. It is being distributed to local schools through State departments of education as an aid in administering Title 3 of the National Defense Act. Additional copies are available at $3.95 from Ginn and Company. Nearly 1000 items of apparatus are listed, along with recommended uses and National Bureau of Standards specifications. The section, "Guidelines" for planning efficient use of laboratory space is excellent. A section on Bibliography for both students and teachers is remarkably comprehensive. This volume does not talk about improvement of instruction, it shows clearly how it can be done.

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

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Sophus Mads Jorgensen (1837–1914)

A chapter in coordination chemistry history

Today most chemists, regardless of their field of specialization, are acquainted with the nature and importance of the work of Alfred Werner. Indeed, practically every freshman chemistry student is now introduced to at least the essentials of his coordination theory. Yet, except for those who have had occasion to delve into the study of complex compounds, the name of Sophus Mads Jørgensen remains entirely unknown.

Few realize that Werner's new and revolutionary theory was based upon experimental data carefully and painstakingly accumulated over a number of years by Sophus Mads Jørgensen, professor of Chemistry at the University in Copenhagen (1871–1908). It is perhaps not an exaggeration to say that Werner's theory might never have been propounded had not Jørgensen's work provided the observations requiring explanation.

Except for some early isolated research, Jørgensen devoted himself exclusively to investigating the coordination compounds of cobalt, chromium, rhodium, and platinum, and this work, upon which his fame rests, forms an interconnected and continuous chain from 1878 to 1906. His interpretations of the luteo, purpureo, roseo, praseo, violeo, croceo, flavo, and other series of complex salts were made in the light of his extensions and modifications of the famous chain theory (*1*, *2*) proposed by the Swedish chemist, Christian Wilhelm Blomstrand (1826–1897).

Jørgensen's views remained essentially unchallenged until 1891 when the twenty-six-year-old Werner published his "Beiträge zur Theorie der Affinität und Valenz." The subsequent controversy between the two men forms an exciting chapter in the history of chemistry and still serves today as a fine example of an ideal scientific discussion.

Yet, despite the obvious importance of Jørgensen's work, no biographical data are available in English with the exception of a short eulogy by one of his most distinguished students, Niels Bjerrum (*3*). It is with a view to filling this gap in the literature of the history of chemistry that this paper is written. The biographical details are taken largely from three Danish articles (*4*, *5*, *6*).

Presented in part before the Division of the History of Chemistry of the American Chemical Society at the 133rd National Meeting, San Francisco, California, April, 1958.

Biography

Sophus Mads Jørgensen was born in Slagelse, Denmark, on July 4, 1837. His early schooling was obtained at Slagelse and later at the *Sorø Velvillie*. At this academy, his interest in chemistry was awakened by F. Johnstrup. This dedicated teacher allowed the older students to work in his own private laboratory on Sundays, and Jørgensen eagerly availed himself of the opportunity.

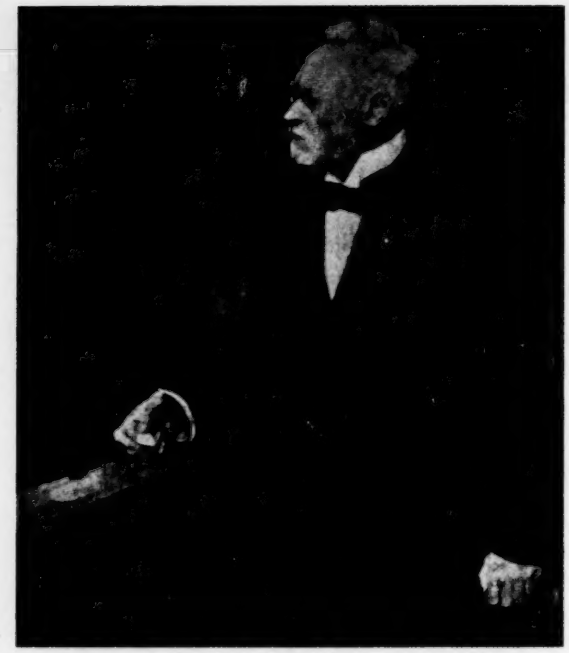
After his graduation in 1857, Jørgensen entered the University at Copenhagen and in 1869 received his doctorate with the dissertation "Overjodider af Alkaloiderne" (Polyiodides of Alkaloids). In 1871 he became *Lektor* at the University and in 1887, Professor of Chemistry, a position which he held until 1908, the year of his retirement. He died on April 1, 1914.

During his 41 years of teaching, Jørgensen exerted a profound influence on a whole generation of Danish chemists and may even be said to have founded a school. Such outstanding men as O. T. Christensen, E. Koefoed, Niels Bjerrum, and S. P. L. Sørensen initiated their research careers under his direction.

Jørgensen always preferred facts to bold hypotheses, and his controversy with Werner clearly reflects this attitude. Niels Bjerrum (*3*) relates how Jørgensen reminded advanced students that although the atomic theory was a useful concept for correlating and explaining a large number of experimental facts, they ought not to think of atoms as actual objects.

Although not actually eloquent, Jørgensen could completely absorb his audience's attention when a subject caught his interest. For example, his lectures on Lavoisier's life and work made a profound impression on his students. In his teaching, he consistently managed to convey to them not only a clear understanding of chemistry, but also a love and respect for the science.

Through his textbooks, Jørgensen was able to extend his teaching influence far beyond the select circle of his own students. These works reflect the same characteristic thoroughness that he expended in his laboratory investigations. Probably his most famous text is "Kemiens Grundbegreben" (Fundamentals of Chemistry), published in 1902. In less than 200 pages, Jørgensen gives not only a summary of the basic concepts of chemistry, but also a survey of its historical development. This little classic has been translated



Sophus Mads Jorgensen (1837–1914), professor of chemistry in Copenhagen (1871–1908). ("*Proceedings of the Symposium on Co-ordination Chemistry, Copenhagen, Aug. 9–13, 1953,*" *Danish Chemical Society, Copenhagen, 1954, p. 14.*)

into several languages, among them German (1903), Italian (1904), Greek (1904), and English (1908).

As a research worker, Jørgensen was methodical, deliberate, and careful. Although he could have delegated much routine work to assistants, he insisted on personally performing all his analyses. In view of his passion for perfection, his output was tremendous, and we are indebted to him for many of the basic experimental facts of coordination chemistry.

In contrast, Werner was a rapid worker who preferred qualitative tests using porcelain plates and watch glasses to more conventional quantitative methods. Niels Bjerrum recalls the following incident typical of Werner's impulsive temperament. When Arthur Hantzsch, Werner's professor, asked him, on short notice, for a paper describing the coordination theory, Werner entered a room with a box full of cigars and did not leave until the paper was written and the cigar box empty (*3*).

Like many famous chemists, Jørgensen was not content merely to make original contributions in the laboratory, but was also keenly interested in the historical development of chemistry, especially in Denmark. His studies in this field are characterized by the same enthusiasm and thorough workmanship shown in his laboratory investigations. Unfortunately, few of these studies have been published.

Jørgensen's strong sense of history caused him to view Werner's new theory as an unwarranted break in the development of the theories of chemical structure. He regarded it as an *ad hoc* explanation insufficiently supported by experimental evidence.

Although unjustly neglected today, Jørgensen's work aroused great interest among his contemporaries. In 1906 the French *Académie des sciences* presented him with its Lavoisier medal. Early in 1907 Henri Moissan, the Nobel prize laureate in chemistry for that year, drafted a proposition to the Nobel committee nominating Jørgensen for the next prize in chemistry. Unfortunately, Moissan died later that year, and the proposition was never submitted.

Nineteenth Century Chemical Confusion

In order to appreciate adequately the magnitude of both Jørgensen's and Werner's achievements, we must take into account the confused state of affairs in which chemistry floundered during most of the nineteenth century. Various rival systems of chemistry flourished. The dualistic theory of Berzelius, which hitherto had been quite successful in the formulation of inorganic compounds, was falling into disrepute as a result of the inroads of the new organic chemistry. No clear distinction was made between equivalent, atomic, and molecular weights. It was only in 1858 that Cannizzaro's revival of Avogadro's hypothesis marked the beginnings of a consistent atomic weight scale. When Cannizzaro spoke at Karlsruhe, Svante Arrhenius had not yet been born. Indeed, years of proselytizing by Arrhenius, van't Hoff, and Ostwald were to be necessary before the electrolytic dissociation theory was finally accepted by the scientific world. Thus, Werner's view of the two types of linkage, ionizable and non-ionizable, did much to clarify ideas of chemical bonding a generation before the views of Kossel and Lewis (1916) led to our present concepts of ionic and covalent bonding.

Today any chemist familiar with modern orbital theory knows that nitrogen can form at most only four bonds. Armed with such knowledge, he might scoff at the apparent naïveté of Blomstrand and Jørgensen whose structural formulas involved chains of ammonia molecules containing quinquevalent nitrogen. Our hindsight is always much better than our foresight. To view the works of great men of the past in the light of modern knowledge is perhaps to belittle their achievements. Thus, in evaluating the work of Jørgensen and Werner, we must preserve a sense of historical perspective.

Werner's coordination theory is familiar to most chemists and need not be elaborated here. However, since Jørgensen's interpretations were all based on the now obsolete Blomstrand chain theory (*1*, *2*), a few remarks about this presently little known theory seem in order.

Odling (*7*) had proposed that the hydrogen atoms in ammonia could be replaced by metal atoms just as they were replaced by organic radicals in forming amines. As an extension of this idea, Blomstrand suggested that these ammonia molecules could link together as —NH_3— chains, analogous to —CH_2— chains in hydrocarbons.

The number of ammonia molecules associated with the metal, i.e., the length of the chain, depended upon the metal and its valence. This point was later accounted for more adequately by Werner's concept of the coordination number. Blomstrand also made provision for different reactivities of various atoms and groups. Thus, halogen which could be precipitated by silver nitrate was called "farther," while that which could not was called "nearer," a close approximation of Werner's later concept of outer and inner spheres.

Jørgensen's Work

Although Jørgensen created no new structural theory of his own, he logically and consistently extended and modified Blomstrand's chain theory to interpret the many new series of complex compounds which he had succeeded in preparing for the first time. Just as astronomers tried to force an explanation for the motion of the planets in terms of the Ptolemaic theory by postulating more and more complicated epicycles, so Jørgensen, in his attempts to account for his newly prepared compounds from a unified theoretical point of view, strained the theory of his mentor Blomstrand to the breaking point. In 1891 the Copernican figure of Alfred Werner appeared on the scene to challenge the old system with a radically new theory based, by Werner's own admission, upon the sturdy foundation of Jørgensen's painstaking experimental investigations. Indeed, Jørgensen's work bore the seeds of the Blomstrand-Jørgensen theory's destruction, for many of the compounds first prepared by him later proved instrumental in demonstrating the validity of Werner's views. One is tempted to compare this situation with Priestley's discovery of oxygen, which led to Lavoisier's classic experiments on the nature of combustion and to the subsequent collapse of the Phlogiston theory. However, unlike Priestley, who staunchly defended this theory until his death, Jørgensen finally became convinced of the correctness of Werner's theory and graciously acknowledged its worth.

Jørgensen's research can be divided into seven groups. The first (1866–1878) includes a few isolated papers and his work on alkaloid polyiodides, while the other six (1878–1906) constitute the work for which he was famous—his investigations of metal-ammine complexes. These studies, entitled "Beiträge zur Chemie der Kobaltammoniakverbindungen" (eight papers), "Beiträge zur Chemie der Chromammoniakverbindungen" (ten papers), "Beiträge zur Chemie der Rhodiumammoniakverbindungen" (nine papers), "Über Metalldiaminverbindungen" (seven papers), "Zur Konstitution der Platinbasen" (four papers), and "Zur Konstitution der Kobalt-, Chrom-, und Rhodiumbasen" (eleven papers) appeared in various publications of the *Videnskabernes Selskab*, then in the *Journal für praktische Chemie*, and after 1892 in the newly founded *Zeitschrift für anorganische Chemie*. Indeed, the fortunate subscriber to this new periodical had a ringside seat for the battle between Jørgensen and Werner.

In the following comparison between Jørgensen's work and that of Werner, we shall concentrate on octahedral hexacovalent ammines of cobalt(III).[1] The survey is organized on the basis of compound type, rather than in strict chronological sequence. First to be considered is type MA_6 in which the coordination number of the central metal atom is satisfied by six ammonia molecules. We shall then proceed to replace the ammonia molecules one at a time with other groups, giving one example from each type.[2]

Type MA_6—Hexammines (Luteo Salts), $[M(NH_3)_6]X_3$. During the first half of the nineteenth century, measurement of vapor density was the only method for determination of molecular weights. Until the classical studies of Raoult and van't Hoff about 1882 on colligative properties of solutions, no reliable method existed for the determination of molecular weights of non-volatile compounds. Thus, cobalt(III) chloride was thought to have the composition Co_2Cl_6 (by analogy with volatile Fe_2Cl_6), and hence cobalt ammines were considered dimers. Jørgensen (*8*) in 1890 and Petersen (*9*) in 1892 deduced evidence for monomeric molecular weights by freezing point and conductivity measurements of such solutions, and Blomstrand's original formulas were halved. Thus, luteo cobaltic chloride, originally written $Co_2Cl_6 \cdot 12NH_3$, was henceforth written $CoCl_3 \cdot 6NH_3$. The concept of octahedral configuration based on coordination number six was a fundamental postulate of Werner's theory from its inception. It is possible that without Jørgensen's halving of Blomstrand's formulas, this theory might never have been conceived.

Luteo cobaltic chloride was found to be a stable yellow-orange compound (*10*). In solution, all the chlorine is immediately precipitated by silver nitrate. Although ammonia is a base, treatment of luteo cobaltic chloride with hydrochloric acid at 100°C does not remove any ammonia. Furthermore, treatment of the solid with sulfuric acid does not remove any ammonia, but yields the compound $Co_2(SO_4)_3 \cdot 12NH_3$, i.e., the chlorine atoms are replaced by sulfate groups. Clearly, some sort of very stable metal-ammonia, but much less stable metal-chlorine bonding is indicated in luteo cobaltic chloride. Blomstrand proposed the symmetrical formula

$$Co_2 \begin{cases} NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \end{cases}$$

On heating, however, one-sixth of the ammonia is lost, and only two-thirds of the chlorine in the resulting purpureo cobaltic chloride can now be precipitated by silver nitrate:

$$[Co(NH_3)_6]Cl_3 \xrightarrow{\Delta} [Co(NH_3)_5Cl]Cl_2 + \overline{NH}_3$$

Removal of two ammonia molecules from Blomstrand's formula for the luteo salt results in a structure which does not sufficiently account for the great difference between the two types of chlorine atoms in the purpureo salt. Therefore, Jørgensen proposed the following symmetrical formula for the luteo salt

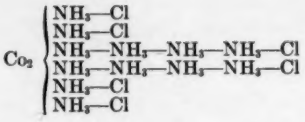
$$Co_2 \begin{cases} NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—NH_3—Cl \\ NH_3—NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—Cl \end{cases}$$

postulating that halogen atoms which are bound to the metal atom through other groups such as ammonia can be precipitated by silver nitrate, while those bound directly to the metal atom cannot (*11*). Since he later regarded four as the maximum number of ammonia molecules that could enter into a chain and since he

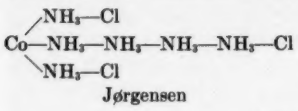
[1] Chapter 2 of J. C. Bailar's "The Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, 1956, has been a valuable source of information in the preparation of this discussion.

[2] For a fuller discussion of Jørgensen's life and work, see KAUFFMAN, G. B., *Chymia*, 6 (1960).

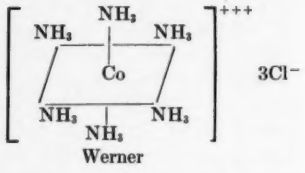
regarded such a chain as a particularly stable arrangement, Jørgensen (*12*) subsequently modified this formula to



Henceforth, all his structural formulas will show this four-ammonia chain although his original proposals were slightly different. Both Jørgensen's[3] and Werner's structures are compatible with the experimental observations but differ in that Jørgensen regarded the chlorine atoms as attached to the metal atom through ammonia molecules, while Werner regarded them as ionic—"at large," so to speak—a concept considered quite revolutionary at that time. Werner also regarded the central metal atom and the ammonia molecules as comprising a discrete unit, a complex cation. Such a structure should yield four ions in solution, and this was later confirmed by the conductivity studies of Werner and Miolati (*13*).



Jørgensen



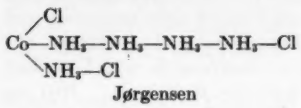
Werner

Type MA_5B—Pentammines (Purpureo Salts), $[M(NH_3)_5X^{-n}]Y_{3-n}$. The term purpureo (purple) is derived from the color of purpureo cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, the substance with which Jørgensen began his research on complexes. This compound is formed by heating luteo cobaltic chloride,

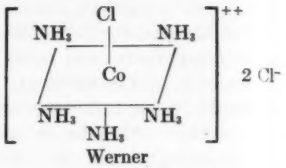
$$[Co(NH_3)_6]Cl_3 \xrightarrow[>100°C]{\Delta} [Co(NH_3)_5Cl]Cl_2 + \overline{NH}_3 \ (10)$$

and thus purpureo salts were regarded by Jørgensen as luteo salts in which one-sixth of the ammonia had been replaced by halogen. The ammonia molecules are quite strongly bound to the cobalt atom in the purpureo salt as shown by the fact that ammonia is not evolved even on heating to 100°C. Furthermore, Jørgensen showed that cold concentrated sulfuric acid did not react with the ammonia in the salt but yielded the compound $[Co(NH_3)_5Cl]SO_4$, which, although it contained chlorine, gave no immediate precipitate with silver nitrate. He also found that only two-thirds of the chlorine in the original salt could be immediately precipitated by silver nitrate, while the remaining third was precipitated only on long boiling (*14*).

To account for this difference in reactivity, Jørgensen suggested, as did Werner after him, that the "unreactive" or "masked" chlorine was bound directly to the metal atom. The structures proposed by these two investigators,



Jørgensen



Werner

are both compatible with the experimental facts but differ again in the mode of attachment of the "reactive" chlorine atoms. Jørgensen regarded these atoms as linked to the metal atom through ammonia molecules, while Werner considered them as not linked to any particular atom, but attracted to the complex cation as a whole by electrostatic forces.

Werner explained the formation of the purpureo salt from the luteo salt by evolution of ammonia as a conversion of one of the three chlorine atoms from a primary (ionic) to a secondary (non-ionic) valency. The entrance of the negative chlorine into the complex cation lowers the charge of the latter by one, and the charge of the resulting complex cation is now two, rather than three. Jørgensen criticized this interpretation, arguing that if a given negative group is coordinated to the central metal atom, it cannot simultaneously satisfy one of the primary valencies of the metal (*15*), a point which Werner (*16*) later clarified. Werner's structure requires that a solution of purpureo cobaltic chloride furnish three ions, a fact confirmed by the conductivity studies of Werner and Miolati (*13*).

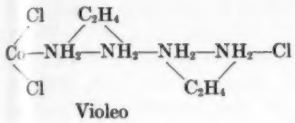
Type MA_4B_2—Tetrammines. These compounds may be regarded as luteo salts in which one-third of the ammonia has been replaced by other groups. It is among such compounds that we first encounter the possibility of stereoisomerism.

Cis- and trans- Dichlorobis(ethylenediamine) Salts (Violeo and Praseo Salts), $[M\{C_2H_4(NH_2)_2\}_2Cl_2]X$. The best known example of *cis–trans* isomerism among inorganic complexes was first observed by Jørgensen not among simple tetrammines, but among salts in which the four ammonia molecules have been replaced by two molecules of the bidentate organic base, ethylenediamine (*17*). He evaporated an aqueous solution of the green compound, praseo cobaltic chloride $[Co\{C_2H_4(NH_2)_2\}_2Cl_2]Cl$, and obtained an isomeric violet compound which he called violeo cobaltic chloride. Treatment of the violeo compound with hydrochloric acid regenerates the original praseo compound. Two-thirds of the chlorine in these compounds is "masked" but becomes ionic in solution as a result of aquation (*18*).

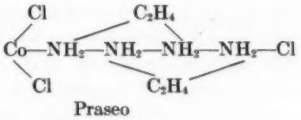
Jørgensen also prepared other members of the praseo (green) and violeo (violet) series as well as many ethylenediamine derivatives of platinum. He regarded the difference in color as due to structural isomerism connected with the linking of the two ethylenediamine molecules. Werner, on the other hand, believed these compounds to be stereoisomers, i.e., compounds with the same atoms and bonds but differing

[3] For simplicity, monomeric formulas will be used for the remainder of this discussion although they were not used by Jørgensen until 1890.

only in the orientation of these atoms and bonds in space:

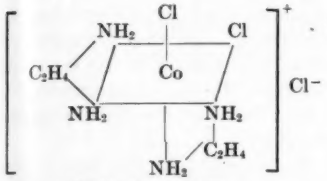


Violeo

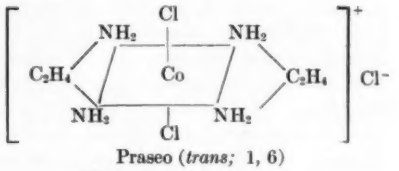


Praseo

Jørgensen



Violeo (*cis;* 1, 2)



Praseo (*trans;* 1, 6)

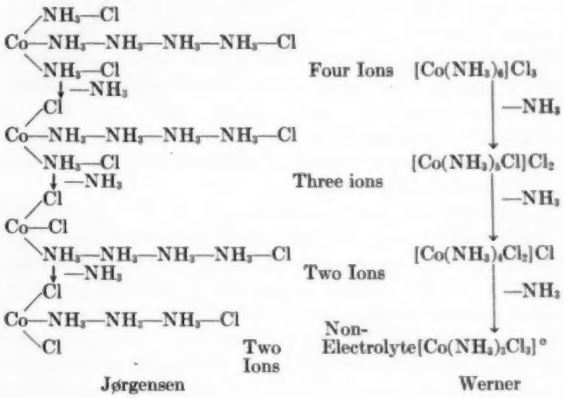
Werner

According to Werner, this isomerism was merely a geometric consequence of the octahedral structure and should be observed in compounds of type MA_4B_2 which do not contain ethylenediamine. Thus, his theory would predict the existence of a series of violeo (*cis*-dichlorotetramminecobalt(III)) salts, $[Co(NH_3)_4Cl_2]Cl$, isomeric with the corresponding praseo (*trans*) compounds. However, replacement of both nitro groups in flavo (*cis*-dinitrotetramminecobalt(III)) salts with chlorine using dilute hydrochloric acid always resulted in formation of the praseo (*trans*) compounds. Naturally, Jørgensen, being a confirmed empiricist, criticized Werner's theory on the ground that it implied the existence of such unknown series of compounds. The apparent non-existence of a violeo (*cis*-dichlorotetramminecobalt(III)) series, however, represented only a temporary victory for Jørgensen since this series was finally discovered by Werner (*19*), who also subsequently explained the formation of *trans* compounds from *cis* compounds by a theory of rearrangements (*20*). Werner further predicted that as a consequence of its asymmetric octahedral structure, the violeo salt should exist in enantiomorphic forms. *Cis*-dichlorobis(ethylenediamine)cobalt(III) chloride was finally resolved into its optical antipodes by Werner (*21*) in 1911 and later by Bailar and Auten (*22*).

Type MA_3B_3—Triammines, $[M(NH_3)_3X_3]^\circ$. These compounds may be regarded as luteo salts in which one-half of the ammonia has been replaced by other groups. This type of compound played a most prominent role in the supersession of the Blomstrand-Jørgensen chain theory by the Werner coordination theory.

So far we have seen how Jørgensen's and Werner's formulations for metal-hexammines, pentammines, and tetrammines, both systems reasonably compatible with experimental facts, permitted two rival hypotheses to exist side by side for a limited time. However, the scientific mind feels uneasy at accepting two alternative explanations for a given group of phenomena, the coexistence of the wave and corpuscular theories of light notwithstanding. As more experimental evidence accumulated, the scales began to tip in favor of Werner's theory.

When successive ammonia molecules in a hexammine are replaced by negative groups such as chlorine atoms, these enter the coordination sphere and thus become non-ionic or "masked." With the replacement of the first two ammonia molecules, the ionic character of the compounds as predicted by the two theories is in complete agreement, but with that of the third ammonia molecule, the ionic character of the resulting compounds differs radically according to the two theories:



Jørgensen predicted that the chain of four ammonia molecules would merely be shortened by one and the resulting compound would be similar to the preceding one in forming two ions in solution, one of the chlorine atoms still remaining ionic. On the other hand, Werner (*23*) predicted an abrupt change in properties. The resulting compound should be a non-electrolyte soluble in non-polar solvents, and such solutions should not conduct an electric current. Werner pointed out that the properties of such compounds agreed with his theoretical predictions. Jørgensen (*12*) protested that the very few triammine complexes of trivalent metals then known were too poorly characterized to allow any conclusions to be drawn.

The classical conductivity studies of Werner and Miolati (*13*) on a wide variety of metal-ammine complexes agreed very well with Werner's theory. The conductivities of compounds such as $[Co(NH_3)_3(NO_2)_3]$ were found to be extremely low, an indication of non-electrolytic character. Petersen (*24*) verified Werner and Miolati's experiments but objected to their conclusions in those cases where the conductivities corresponded to a greater number of ions than that predicted by the coordination theory. Werner explained these apparent discrepancies by aquation reactions such as

$$[Co(NH_3)_3(NO_2)_2Cl]^\circ + H_2O \longrightarrow [Co(NH_3)_3(NO_2)_2(H_2O)]^+ + Cl^-.$$

However, measurements of compounds not containing as ligands groups readily displaced by water agreed completely with the theory. Petersen also tried to verify his conductivity measurements by cryoscopic studies, but he encountered some discrepancies. Jørgensen (*15*) seized upon these in an attempt to discredit the entire conductivity method and hence all of Werner and Miolati's results. Actually, Petersen's results did not support Jørgensen's view any better than they did Werner's theory.

Conclusion

It was only natural that Werner's views, marking a sharp break in the classical theory of valency and structure, should have seemed too radical to Jørgensen. When Werner first proposed his theory, the octahedral configuration for cobalt(III) was a mere guess without adequate experimental verification. At this time, on the other hand, the older man had already devoted many years to thorough investigations of metal-ammine complexes and had accounted for his findings by a consistent application of Blomstrand's chain theory, which he modified, but only when absolutely necessary. However, when Werner (*19*) in 1907 finally succeeded in preparing the missing violeo (*cis*) series of dichlorotetramminecobalt(III) salts whose existence was a necessary consequence of his theory, but not of Blomstrand's, Jørgensen promptly acknowledged the validity of Werner's views.

Another necessary consequence of the octahedral configuration was the fact that compounds of type $M(AA)_3$, i.e., compounds in which the coordination number of the central metal ion is fulfilled by three symmetrical chelate groups (which can only span *cis* positions), should be optically active. When Werner in 1912 succeeded in resolving into optical antipodes compounds of type $[M\{C_2H_4(NH_2)_2\}_3]X_3$ of cobalt(III) (*25*), chromium(III) (*26*), and rhodium(III) (*27*), the correctness of Werner's views became all the more apparent to Jørgensen. Yet because of the prevalent view that optical activity was connected with carbon atoms, a number of Werner's contemporaries objected that the optical activity was due to the ethylenediamine molecules, even though these are optically inactive. Finally, in 1914, when Werner (*28*) succeeded in resolving the completely inorganic compound dodecammine-μ-hexol-tetracobalt(III) bromide

$$[Co\{\begin{matrix}OH\\ \diagup\ \diagdown\\ OH\end{matrix}Co(NH_3)_4\}_3]Br_6,$$

using silver dextro-α-bromocamphor-π-sulfonate, even his most sceptical opponents were silenced, and the octahedral configuration of cobalt(III) was unequivocally established. Ironically, this compound, which forged a crucial link in the proof of Werner's coordination theory, was first prepared by Jørgensen (*29*), the foremost exponent of the rival Blomstrand chain theory.

The controversy between Jørgensen and Werner over the constitution of metal-ammine complexes provides us with an excellent illustration of the synergism so often encountered in the history of science. During the course of this competition, conducted without any trace of jealousy or rancor, each chemist did his utmost to prove his views, and in the process a tremendous amount of fine experimental work was performed by both. Although not all Jørgensen's criticisms were valid, Werner, in many cases, was forced to modify various aspects of his theory. However, the basic postulates were verified in virtually every particular.

Although Werner's ideas eventually triumphed, Jørgensen's experimental observations are thereby in no way invalidated. On the contrary, his experiments, performed with extreme care, have proven completely reliable and form the foundation not only of the Blomstrand-Jørgensen theory, but of Werner's as well. From the very beginning of the controversy, Werner continually acknowledged his great debt to the older man. For example, in 1913, on his return to Zurich from Stockholm where he had received the Nobel prize, Werner addressed the *Kemisk Forening* in Copenhagen, acknowledging the important role that Jørgensen's experimental contributions had played in the development of the coordination theory. Unfortunately, Jørgensen's grave and final illness prevented the meeting of the two great adversaries.

Eduard Farber, on the occasion of the hundredth anniversary of Wilhelm Ostwald's birth, discusses Ostwald's twofold division of scientific genius (*30*). This dichotomy seems particularly applicable to Jørgensen and Werner. In Jørgensen, the conservative, we have the classic type, the slow and deep-digging completer who produces with long deliberation and slowly develops a traditional theory to new consequences. In Werner, the liberal, we have the romantic type, the impulsive and brilliant initiator who produces prolifically and easily at an early age. Each needs the other. Science has need of both.

Acknowledgment

The author wishes to acknowledge the assistance of Professor Niels Bjerrum of the *Kgl. Veterinaer-og Landbohøjskoles kemiske Laboratorium*, Københavrn, in locating the Danish biographical articles. He is also indebted to Finn Inge Grønberg of Fresno State College for help in translating these.

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A Simple Katharometer Design

With the rapid growth of the gas-chromatographic technique in recent years, there has been a parallel emphasis on the design of thermal conductivity cells (katharometers) for use as detectors. The design theory for hot-wire katharometers has been discussed thoroughly (*1*, *2*, *3*), and information on the characteristics of thermistors also is readily available (*4*). However, the actual construction of a satisfactory katharometer often requires skillful use of glass blowing or machine shop practice. In order to circumvent these construction difficulties, the simple katharometer shown in the accompanying figure was designed. No glass work is required and the only necessary tools are a drill, hacksaw, file, tap, and soldering facilities.

The katharometer block is cut from a piece of brass rod stock. Axial holes, $^1/_8$-in. in diameter, are drilled to provide gas paths. At one end of the block the holes are reamed for a short distance with a larger drill and then tapped to accept standard brass fittings. The gas paths for the reference and the sensing sides are identical and are as indicated by the arrows, *W*. The up and down paths for each half of the cell are joined by flat brass caps, soldered to the katharometer block at *Z*. The horizontal path in each cap is prepared by chemical etching after masking the piece with paraffin. The additional time of gas residence within the block provided by the U form of the path allows the sample to come to temperature equilibrium with the katharometer.

Holes are drilled from the side of the block to accept premounted matched filament (*5*) or thermistor (*6*) detectors. For our work, thermistors were used. The volume of each thermistor cavity was approximately 0.6 ml. The thermistor flanges were backed at *X* with plugs of Sauereisen cement.

For operations at room temperature or below, a copper cooling coil can be soldered directly to the katharometer block. For high temperature operation an electric-cartridge heater (*7*) and a regulating device (*8*) may be inserted into two holes drilled directly into the block.

This katharometer was designed in connection with work supported by the U. S. Atomic Energy Commission.

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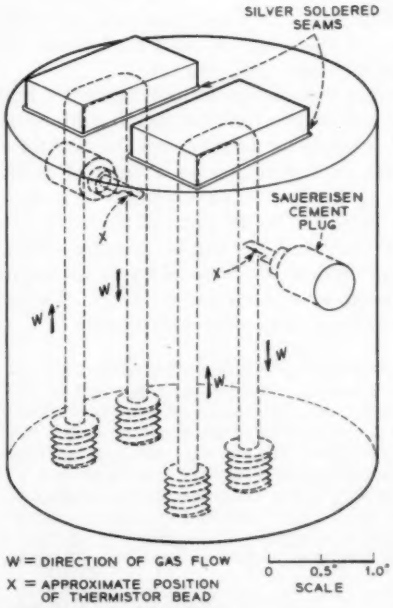
The katharometer was constructed originally for studies on the chromatographic separation of hydrogen isotopes (*9*). However, the design should be applicable for a variety of problems.



Katharometer for gas chromatography.

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Vapor Density Apparatus for General Chemistry Laboratory

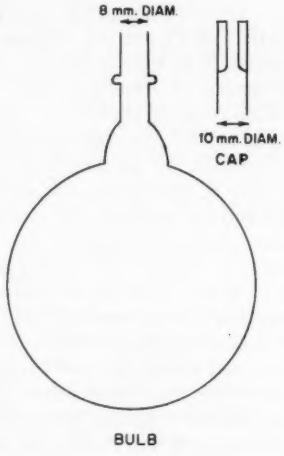
The apparatus commonly used in general chemistry to determine molecular weights of volatile liquids consists of a flask fitted with a cork stopper equipped with a capillary escape tube. The cork may be wrapped in aluminum foil to reduce absorption of vapor. Modifications of this apparatus which avoid the use of a stopper have been described.[1, 2, 3] An error which seems to have received less attention is caused by evaporation of condensed liquid while the flask is being cooled and weighed.

The apparatus shown in the figure is designed to eliminate errors due to absorption and evaporation. The bulb is made by drawing out the neck of a 200-ml Pyrex flask and sealing it to a piece of glass tubing. The tube is compressed at one point to form a ring so that the bulb can be suspended from the arm of an analytical balance. The cap is made by sealing a piece of capillary tubing to a piece of Pyrex tubing just large enough to slip over the top of the bulb. The volume of the bulb is determined and marked on it.

A cork stopper is inserted in the top of the bulk which is then weighed to ±0.001 g. The stopper is removed, a few milliliters of liquid added, and the cap slipped into place. The apparatus is clamped in a water bath so that the water level is at the narrow section of the bulb. The water is boiled gently for five minutes after all the liquid appears to have veen volatilized. The cap is then slipped off and the cork stopper quickly inserted. The flask is cooled to room temperature and the stopper removed momentarily to allow air to enter. The stopper is reinserted; the bulb is wiped off and weighed, and the molecular weight calculated.

Diffusion of vapor or steam through or around the cap is negligible unless heating is extended for more than 15 minutes after the liquid has been volatilized. A small amount of vapor may escape while the cap is being replaced by the stopper. So long as this exchange is carried out rapidly, the loss is insignificant. There is no tendency for vapor to escape when the stopper is removed momentarily since air flows into the partially evacuated bulb at this point.

Two or more determinations can be carried out in a 3-hour period. The apparatus is easily cleaned by evacuating with a water aspirator. The bulbs are quite sturdy; 300 students using 40 bulbs over a one week period broke only one of them.



Special apparatus.

The accuracy and precision of this experiment were checked with a class of 600 students using 5 liquids boiling from 60–84°C as unknowns. Half of the students used the apparatus shown in the figure; the others used an Erlenmeyer flask fitted with a cork stopper wrapped in aluminum foil. The molecular weights reported were corrected for deviations of the vapor from ideal gas behavior and for the air displaced by vapor in the final weighing.

With carbon tetrachloride, the median molecular weight using the special apparatus was 156; the conventional apparatus gave a value of 150 (theoretical = 156). The poorest results were obtained with the lowest boiling liquid, isopropyl bromide, which gave medians of 119 and 114, respectively (theoretical = 123). The comparative precision of the two methods is indicated by the fact that 54% of the molecular weights obtained with the special apparatus were within ±3% of the median while only 18% of those obtained using Erlenmeyer flasks were within this range.

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Report of Subcommittee for Improving Secondary School Chemistry

A task assigned this committee was the preparation of a "summary of the many programs and proposals concerned with the improvement of chemical education in the high schools." The following list enumerates those programs considered by the committee to be significant in scope and impact:

Educational Conferences and Institutes (1959)

NSF Institutes and Conferences for high school teachers.
NSF Summer Research Experience Appointments for high school teachers.
Reed College and Wesleyan University Conferences (ACS Division of Chemical Education).
Reports of NSTA Conferences at San Jose State College and Swarthmore College.

Teaching Aids

MCA open-ended chemistry laboratory experiments (available free upon request).
ACS-NSTA Tests in High School Chemistry.
The results of the experience in teaching chemistry by TV in Cincinnati, Baltimore, and Rochester.
"Chemistry, an Introductory Course," 160 lecture-laboratory sessions on film by John Baxter, produced by Encyclopedia Britannica Films.
MCA and other films.
Twenty-one filmstrips in chemistry; 12 others in preparation from McGraw-Hill Educational Films.
Atomic- and ionic-size charts and the expanded chart form of the Periodic Table.

Curriculum Studies

The NSTA committee has studied new developments in science curricula.
A chemistry course based on bonding is being studied at the present time (information available from Prof. L. E. Strong, Earlham College, Richmond, Indiana).
This committee suggests also considering other approaches such as:
The periodic arrangement.
Major principles.
The historical approach (case histories).
Organic and biochemistry.
Revision of commercially published high school textbooks by their authors and editors should be considered.

Local Aid-to-Education Programs

Radio and TV programs by the several ACS Sections (see *C & E News* for listing).
Participation of local sections of ACS, AIC, SM in high school programs (contact local officers).
Participation of chemical employees in chemical education through MCA and chemical companies (contact public relations department of companies).

ROBERT H. CARLETON, *chairman*
ROBERT E. HENZE
ELBERT C. WEAVER

Crossword Puzzle

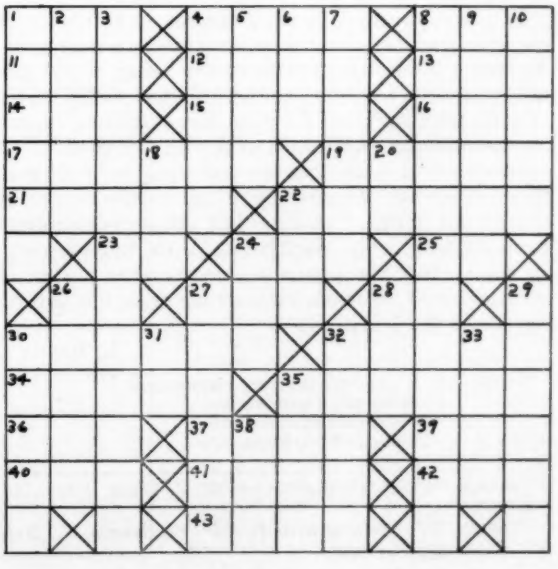
Bert H. Clampitt
Wichita, Kansas

Across

1. State of matter
4. ——— energy
8. Pastry
11. Unit of electric current
12. Boyles and Charles ———
13. 198 inches
14. An untruth
15. 100 square meters (plural)
16. Formic acid is a ——— carbon acid
17. Surround
19. Developed mass spectrograph
21. Cry of horse
22. Spectral series
23. Iron
24. Symbols for frequency
25. Cerium
26. Lithium
27. Particle in a ———
28. Lieutenant (abbreviation 30). 10^{-6} meters
32. Salt containing oxygen
34. $(C_2H_5)_2O$
35. Compounds containing $—NH_2$
36. Golf mound
37. Hindu God
39. Party holding office
40. Age
41. Rare gas
42. Employ
43. 45 inches (plural)

Down

1. Lead sulfide
2. Compound containing $—NH_2$
3. $(\partial H/\partial T)_P$ (two words)
4. ——— point
5. ——— earth
6. Female sheep
7. Literary composition
8. 5*f* rare earth element
9. Citrylidiene acetone
10. Paradises
18. Era
20. Samarium
22. Lumen per square meter
24. ——— metal
26. 1000 cubic centimeters
27. Boron hydride
28. 61 (Roman)
29. ——— function
30. 100 centimeters
31. Rhenium
32. Signs
33. Lairs
35. p-propenylphenol
38. Coagulated sol



Chem Ed

LETTERS

To the Editor:

When using aspirator pumps the water splashing has always been a nuisance.

A simple method to prevent this is to remove the asbestos from a 4 × 4 in. wire gauze, asbestos centered.

Press the wire into the drain outlet to raise the center of the wire. Place the wire in the sink directly under the aspirator and the splashing will be at a minimum.

DANIEL BORYTA

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To the Editor:

In the June, 1959, issue of THIS JOURNAL, Morimoto and Kahn[1] described simple equipment to make carrier-free radioactive lead 212 (thorium B). They use solid thorium hydroxide as an emanating source and collect the thorium B in an electric field.

Some years ago, we described another method for making carrier-free thorium B, which is even simpler.[2] The method consists essentially in passing a current of air through a sinter into a flask containing a saturated solution of thorium nitrate in equilibrium with its decay products. The air takes up some of the thoron and then carries it through a second flask filled with dilute acid. Part of the thoron dissolves in the acid and decays there (half life 54.5 sec) to give first short-lived thorium A and subsequently thorium B.

It was shown that in the given set-up a velocity of the air current of about 5 ml/sec gave optimum yield. Activities of the thorium B of the order of 10^5 disintegrations per minute can be obtained easily. This is more than sufficient for most demonstration experiments and for much research work with radiolead.

However, if even greater activities were desired, these could be obtained by using as the source of thoron not ordinary thorium but either radiothorium or mesothorium in equilibrium with radiothorium. In these cases, the production rate of gas per ml of solution could be much higher than with the natural mixture of thorium isotopes.

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[1] MORIMOTO, E. M., AND KAHN, M., J. CHEM. EDUC., **36**, 296 (1959).

[2] BRODA, E., FABITSCHOWITZ, H., AND SCHÖNFELD, T., *Monatsh. Chem.*, **83**, 482 (1952).

To the Editor:

As a result of many demonstrations of "The Nylon Rope Trick" (J. CHEM. ED., **36**, 182 (1959)), there has been devised a variation of this polycondensation experiment which is dynamic and yet does not require winding devices. It is continuous and self-propelled.

A satisfactory way to get a spontaneous flow of film is to conduct the collapsed film from the center of the vessel over a glass rod or tube and then out and down over a second rod. A fall of about three to four feet is necessary for the film to flow continuously. The required height depends on the size of the vessel, the solvent and reactant system, and the distance of the aqueous surface from the guide rod. Figure 1 shows a simple way of arranging guides from wire and medicine droppers. The main requirement for easy flow is a very smooth inert surface.

The length of time during which the film will form continuously depends on the components and the physical dimensions of the system. A preferred recipe is 1.5 ml sebacoyl chloride in 50 ml perchloroethylene and 2.2 g hexamethylenediamine and 4.0 g sodium carbonate in 50 ml water. These reactants in a 200-ml tall-form beaker ($2^1/_4$ in. i.d.) will produce film for 8 min at about 14 ft/min. Speeds up to 60 ft/min can be obtained by allowing the rope to fall a greater distance. The flow of rope can be stopped by pushing it to the ends of the guides or against the wall of the beaker or by reducing the length of overhanging rope. The flow can be resumed by centering the rope on the guides and giving it a pull.

Figure 1.

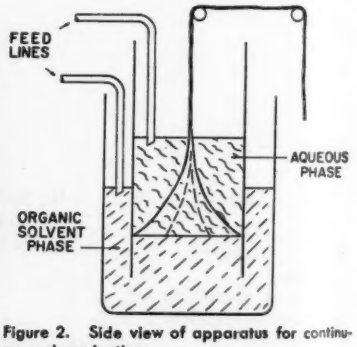

Figure 2. Side view of apparatus for continuous polymerization.

For the purpose of a long exhibition the process can be continued by arranging separatory funnels and tubing as reservoirs from which to replenish the phases. The feed line for the lower phase should not go *through* the interface. It must enter through the wall of the vessel below the interface or be cemented smoothly to the inside of the vessel so securely that no liquid goes behind it. An alternative arrangement is shown in Figure 2 wherein the aqueous phase is placed inside a large open tube supported in a somewhat larger vessel containing the organic solvent. Both phases may then be replenished externally.

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Chem Ed

BOOK REVIEWS

Nuclear Magnetic Resonance

John D. Roberts, Professor of Organic Chemistry, California Institute of Technology. McGraw-Hill Book Co., Inc., New York, 1959. viii + 118 pp. Figs. and tables. 16 × 23.5 cm. $6.

Any effort to translate the principles of a field such as magnetic resonance, which properly belongs on the research frontiers of modern physics, into less mathematical language suitable to the average organic chemist deserves our attention and support. Professor Roberts has on the whole been successful in presenting such a translation with little loss in rigor, and he has made clear the wide range of interesting organic chemical problems to which the techniques of nuclear magnetic resonance (NMR) can be usefully applied. (No doubt most of the future development and use of NMR will be carried out by chemists, simply because they are more aware of the problems susceptible to attack by the method.)

Roberts' Preface states that the "coverage is illustrative rather than comprehensive," and this statement characterizes the book. It will not make the reader a capable operator of NMR equipment, nor will it make him an expert on the interpretation of the data. The first two chapters discuss the phenomenon of NMR and the nature and determination of the chemical shift parameter, which is the measurable quantity of greatest interest to the chemist. The treatment of nuclear relaxation and the characteristic relaxation times in chapter one is the best qualitative discussion of these topics which the reviewer has seen. Appendix A contains a treatment of the Bloch equations for NMR line shapes, given in sufficient detail to avoid the usual gaps which are supposed to be "obvious" to the reader of such derivations. A series of plots of the phase relations of the radio frequency signal and the induced field at the receiver coil under various conditions of RF signal leakage is used to demonstrate with admirable clarity how the equipment must be operated to detect a pure absorption signal.

Chapters three and four describe the use of spin-spin splittings in the determination of structure and the application of NMR to studies of reaction kinetics. They successfully indicate the scope of these applications to organic chemistry (but not its other branches), and suggest some of the pitfalls in the interpretation of NMR spectra. Chapter 5 is a brief discussion of nuclear electric quadruple effects and the highly specialized double resonance technique.

Appendix C contains twenty problems on the determination of structure from the molecular formula and NMR spectrum of an unknown compound. Some of these depend upon rather specialized points mentioned briefly in the text, and the calculation of chemical shifts is handicapped by an error in the units used in the fourth column of Table 1-1, which lists the proportionality constants relating magnetic field strength and frequencies which induce resonance. The column is headed "megacycles per kilogauss," but the correct unit is megacycles per ten kilogauss, as stated on page 18.

Roberts' book is the best available brief introduction to the principles and particularly to the organic chemical applications of NMR. His treatment of these topics is adequate for the requirements of the working organic chemist or for the student who wants to know what NMR is and what it can do. More rigorous and detailed discussions are available, and would be necessary for anyone planning active work in the field; references to these are collected in Appendix B.

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Phosphorus and Its Compounds. Volume 1: Chemistry

John R. Van Wazer, Assistant Research Director, Inorganic Chemicals Division, Monsanto Chemical Co., St. Louis, Missouri. Interscience Publishers, Inc., New York, 1958. xii + 954 pp. Many figs. and tables. 16 × 23.5 cm. $27.50.

The author's stated purpose in this book is "to lay a foundation for a new separate discipline—phosphorus chemistry." Some unifying principles are stated, such as the stability of quadruply connected phosphorus as compared to triply, and quintuply connected phosphorus. Some comparisons are made for carbon, silicon, and phosphorus, with respect to bonding, catenation, and rates of reaction. However, after the book is digested, it seems questionable to the reviewer whether phosphorus chemistry will prove to be sufficiently unique to permit the establishment of a separate discipline.

The author has made no attempt to "review exhaustively the literature of phosphorus and its compounds," but the 889 pages of text and appendixes, and more than 3000 literature citations (some duplication from chapter to chapter), atests to the fact that a tremendous volume of literature has been covered, (through part of 1957). Certainly this volume is a very important contribution to the study of phosphorus chemistry. The author is to be complimented for taking on and sticking to such a herculean task. A second volume on the technology, functions, and applications will follow.

In the first three chapters the ground work is laid for the discussion of the detailed chemistry of the following chapters. These chapters contain some of the simplest concepts of chemistry presented in unusual detail for this type of book. For instance, "electrons are diffuse negative charges with essentially no mass," "these superscripts add up to 15" (in the electronic configuration of the neutral phosphorus atom), and the discussion of ionic and covalent bond on page 10. On the other hand, some of the more advanced physical chemical principles are presented in a brief and approximate fashion. In Chapter 2 the relationship between π-bond character and bond distances is developed, and although the author comments that "this does not, however, show that π-bonding is the common cause for ob-

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served bond shortenings and excess enthalpies" (p. 42), he uses the concept extensively through the book without further comment. Chapter 3 contains the foundations on which the detailed chemistry is developed and it is important as a summary of the author's philosophy of phosphorus chemistry. The chapters all start with a brief historical introduction followed by a detailed presentation of data from the literature.

Chapter 4 covers elemental phosphorus and phosphides; Chapter 5, the chemistry of the hydrides, halides, and pseudohalides, and their organic derivatives; Chapter 6, the oxides, sulfides, nitrides, and related compounds; and in Chapter 7 the lower oxyacids of phosphorus, their salts, and esters. Much of the author's own published work appears in Chapters 8, 10, 11, and 12, which covers the structure and properties of condensed phosphates, individual chain phosphates, ring and branched phosphates, and amorphous phosphates including phosphate glasses, condensed phosphoric acids, and phosphate esters. Chapter 9 covers orthophosphoric acid, its salts, and esters and it contains a detailed discussion of calcium orthophosphates. Chapter 13 contains information on halo-, peroxy-, thio-, and amido acids of phosphorus. The book is completed with three appendixes, one listing data on phosphate minerals, the second, a collection of single bond distances and energies for use in calculations concerning phosphorus compounds, and the third a collection of thermodynamic data on phosphorus compounds.

There are few errors of fact, and some cases of too many literature references keyed to one sentence, with the result that the sentence does not accurately reflect the content of the papers. Each individual reader, especially those working in phosphorus chemistry will find statements to challenge concerning the interpretation of data, and the results of the author's speculation, because he makes his points quite emphatically. Exclamation points are used freely! The book contains a wealth of structural data, some of which is based on nuclear magnetic resonance results. There are also many phase diagrams, and considerable information on the physical properties of phosphorus compounds. For its size, the book is amazingly free of typographical errors. All in all it is an excellent source of reference material.

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No More War!

Linus Pauling, Professor of Chemistry, California Institute of Technology. Dodd, Mead and Co., New York, 1958. ix + 254 pp. 14.5 × 21 cm. $3.50.

When 11,000 scientists of 49 countries petition the United Nations to stop nuclear testing it is newsworthy. When 37 of those petitioners are found to be Nobel Laureates, science teachers should be impressed. But when highly regarded scientific apologists for the United States program of nuclear testing discount the fears of those thousands of petitioners the public, maybe even the science teacher, is understandably confused. "No More War!" is addressed to the confused public.

In ten chapters, starting with an introductory, The End of War, there follows: The Nature of Nuclear Weapons; Radioactive Fallout; Radioactivity and Heredity; Radiation and Disease; The Facts about Fallout; Nature of Nuclear War; Scientists Appeal for Peace; Need for International Agreements and a Proposal; Research for Peace. Four appendixes contain two appeals by Albert Schweitzer; the declaration of the Nobel Laureates and a listing and classification of the signers of the United Nations petition.

A brief bibliography of pertinent books and journals and a double columned seven page index add to the book's offering for those who would return to it for specifics. For those who are less than up-to-date on nuclear science the first two chapters are especially helpful.

Aspects of the current controversy that receive especial scrutiny are: the illusion regarding clean bombs, the scarcity of public information regarding the superbomb, the disregard of the cumulative build-up of radioactive poisoning in the human system, and the public apathy toward the generic long-range menace of radioactive fallout. That which has the least general agreement has to do with the effects of fallout upon germ plasm. It is conceded that it may now be too early to draw more than tentative conclusions on germ plasm mutations. However, when such seasoned generalizations are fully accepted it may be too late to repair the damage already wrought.

This book is not altogether pleasant reading and the reader may not fully agree with all that is said. However, he may, by its help, escape from what the author calls "a protecting cloud of reassuring verbage." The horrors of nuclear war and the menace of nuclear testing will no longer be "something far away."

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History and Philosophy of Science

L. W. H. Hull. Longmans, Green & Co., Inc., New York, 1959. xi + 340 pp. 66 figs. 16 plates. 15.5 × 22.5 cm. $5.

The title of this book is somewhat misleading. It is actually a history of the development of the scientific method. As such it includes much of the history of science, especially for the earlier periods, and a considerable amount of the elementary philosophy of science, including the relation of this specialized branch to the wider cosmological problems which the great philosophers of the past have attempted to solve. The changes in the relationship of science and religion over the centuries are discussed in some detail.

The sections on Greek science are devoted largely to the development of mathematics and astronomy, and well show how the basic principles of scientific method came from these sciences. The development of mechanics in the Renaissance period is well treated, and the gradual change in philosophical outlook as scientific ideas assumed a more dominant position is clearly shown. The influence of the separation of the separate sciences of chemistry in the eighteenth and biology in the nineteenth centuries and their effect on society are discussed. Although the details of the development of chemistry are not given, there are few chemists who will not profit by reading this book.

The illustrations are excellently reproduced, but one serious error is made. We are shown pictures of the busts of such immortals as Hippocrates, Aristotle, and Archimedes as though these were authentic representations. The late George Sarton has often discussed the historical inaccuracy of such a procedure. A note of what must be conscious humor is introduced in the plate of the portraits of the four great evolutionists of the nineteenth century, on the overleaf of which are the portraits of four anthropoid apes.

Although this book does not go deeply into either the history or the philosophy of science, it does correlate these subjects in a manner which is always interesting and stimulating. It should be of the greatest value to young scientists who have been exposed only to technical courses in their own fields. Such readers will find a whole new world opening to them, and many of them may be stimulated into becoming something more than mere technical experts.

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The Pirotechnia by Vannoccio Biringuccio

Edited by *Derek J. Price*, Institute for Advanced Study. Translated from the Italian with an introduction and notes by *Cyril Stanley Smith* and *Martha Teach Gnudi*. Basic Books, Inc., New York, 1959. xxv + 477pp. 94 figs. 20 × 27 cm. $8.50.

The "Pirotechnia" was first published in 1540; it was the first printed work to cover the whole field of metallurgy. Its importance was evidenced by the subsequent appearance of numerous editions in Italy, France, Germany, England, and now in the United States. These are discussed in considerable detail by the present translators and editors. This latest translation is the first complete translation of the "Pirotechnia" into English. It appeared first in 1942, was reprinted in 1943, and this 1959 issue is a photographic copy of the 1943 printing, in which a few typographical errors have been corrected and the index extended somewhat. The volume is beautifully printed and comes boxed.

In harmony with the title, this text deals with the application of heat in the field of metallurgy and related areas. Among the chief topics are mining, working of ores, assaying, alloys, casting (particularly of bells and cannon), prep-

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